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RESEARCH LABORATORY

FINAL TECHNICAL REPORT

CHEMICAL CORROSION OF ROCKET LINER
MATERIALS AND PROPELLANT
PERFORMANCE STUDIES
VOLUME ONE OF TWO

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ABSTRACT

The theoretical equilibria resulting from corrosion of refractory nozzle materials by hot combustion gases have been determined for a number of systems of interest. The refractories considered have include graphite (C), tungsten (W), TaC, HfN, TiC, ZrC, ZrB₂, MgO, and HfO₂. The bulk of the corrosion studies have been performed for "pure" species of arbitrary composition, including AlF₃, BF₂, BF₃, BOF, HBO₂, BeF₂, CO, CO₂, HCl, HF, H₂, H₂O, LiF, N₂ and condensed Al₂O₃ and LaO. Several real propellant systems also have been investigated. In general, corrosion effects have been determined for temperatures in the range 1500-5000°K, and for a nominal total pressure (usually 1000 psia).

The results of these studies have been interpreted in terms of a "saturation number", defined as the mass of wall material required to saturate a unit mass of reacting gases. Saturation numbers have been determined both for "isothermal" and for "adiabatic" conditions. Under certain idealized conditions the saturation number divided by the density of the solid is directly proportional to the linear rate of regression of the surface under attack, and the "adiabatic saturation temperature" becomes the steady-state temperature of the surface, allowing for corrosion heat effects.

Comparing the different refractories on this basis, tungsten (W) and graphite (C) generally rank the most resistant of those materials considered. Tungsten has an advantage over graphite for combustion systems containing oxygen or hydrogen, while the reverse is true for systems based upon fluorine. Tantalum carbide (TaC) also is reasonably resistant to attack by many systems. No material considered, however, was capable of withstanding high-temperature attack by severely oxidizing atmospheres, such as CO₂ and H₂O.

A limited comparison between measured rates of graphite nozzle erosion and rates predicted from a simplified equilibrium model also has been made. At the wall temperatures typical of short firings with state-of-the-art solid propellants, reaction rates apparently are not sufficiently rapid to achieve equilibrium; the predicted erosion rates were high by an order of magnitude or so. The simple equilibrium model may show somewhat greater promise for higher-temperature systems, but even in this case it no doubt would have to be modified to allow for non-unity Lewis and Prandtl numbers.

Theoretical performance calculations previously conducted for unclassified and classified liquid bi-propellant systems also are cited and referenced.

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SECTION 1

INTRODUCTION

This is Volume I of the Final Report in a program which has had two objectives, the first being the theoretical appraisal of various refractory rocket liner materials from a thermochemical standpoint, and the second being the computation of theoretical performance of certain rocket propellant combinations. Chemical corrosion studies reported in the First¹, Second², Third³, Fourth⁴, and Fifth⁵ Quarterly Reports are summarized in this volume. Reference here also is given to the propellant performance studies presented in Volumes II⁶ and III⁷ of the Second Quarterly Report. The thermodynamic data developed for new heavy metal combustion species and presented in the first three Quarterly Reports^{1,2,3} on the other hand, represent a possible area of separate interest, and accordingly have been compiled in Volume II of this report.

In Section 2 of this volume, the assumptions and theory leading to the simplified equilibrium corrosion model are reviewed, including derivation of the "saturation number" as an approximate measure of potential chemical attack. The computer program employed at Aeronutronic to calculate such numbers for both "isothermal" and "adiabatic" conditions is described, and sources of thermodynamic data (apart from those compiled in Volume II) are given. The individual corrosion systems investigated during the course of this work are reviewed, indicating those refractory

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materials considered with certain "pure" species and those considered with real propellant systems.

In a departure from previous presentations of theoretical corrosion results, different refractory materials are compared for given corrosive atmospheres in Section 3 of this volume. In general, nine separate refractories are considered in combination with up to fourteen different "pure" species, from which results relative ratings are derived and discussed. Comparisons also are shown for rocket nozzle materials attacked by five real propellant combustion systems.

The comparisons between rates of nozzle erosion predicted by the simple equilibrium model, calculated by Jones and Delaney⁸, and measured by NASA-Lewis⁹, previously presented in the Fifth Quarterly Report⁵, are reviewed in Section 4 of this volume. Theoretical performance calculations also previously performed are cited in Section 5. Errata for previous reports are given in the Appendix.

SECTION 2

CHEMICAL CORROSION STUDIES

2.1 EQUILIBRIUM SATURATION MODEL

2.1.1 GENERAL CONSIDERATIONS

The theoretical studies of chemical corrosion of refractory rocket liner materials by hot combustion gases, as carried out under this contract, have been based upon the assumption of complete thermochemical equilibrium at the gas-solid interface. Kinetically limited reactions, such as are known to occur at lower temperatures, both homogeneously in the gas phase and heterogeneously with the refractory wall, thus have been excluded from the analysis. Physical erosion by virtue of such effects as aerodynamic shear, thermal shock, and liquid run-off likewise has not been considered. While it is recognized that the simplified model assumed may lead to errors of as much as an order of magnitude or more in certain situations, it is felt that this approach may be of value as a preliminary, relative measure of corrosion resistance for use in screening purposes.

Under the assumption of thermodynamic equilibrium, the stability of a refractory material exposed to a given combustion atmosphere may be expressed in terms of the quantity of refractory required to "saturate" a unit mass of reacting combustion products. The term "saturation" is meant to encompass all possible gas-solid or condensed phase-solid reactions

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forming either gaseous or condensed reaction products, plus any simple vaporization/dissociation of the material in question. Indeed, if the overall "vapor pressure" of the refractory material by itself should exceed, at a given temperature, the total pressure of the system, saturation could never be reached. (Thus, unstable ablative plastics are not covered by the model.) On the other hand, it is possible for a combustion mixture containing the same elements as the refractory to exceed saturation in advance, so that deposition rather than corrosion theoretically would be expected. Just as negative erosion would be predicted for the case just cited, positive or net erosion would be calculated for corrosion reactions forming solid products, even though such products in reality might form a protective layer over the refractory surface.

2.1.2 "ADIABATIC" SATURATION CONDITIONS

The "saturation number" of a refractory material in a given mixture (i.e., the mass of wall material required to saturate a unit mass of combustion products) can be defined either for "isothermal" or for "adiabatic" conditions, and has been denoted by "A" and by "B", respectively, in previous reporting under this contract. More generally, however, the designation "B" is used for the saturation number under conditions not necessarily specified. The definition of the "isothermal" saturation number "A" for a fixed temperature and pressure is unequivocal, depending only on basic thermodynamic considerations. The concept of the "adiabatic" saturation number, on the other hand, does involve a relationship between bulk flow conditions, saturation conditions at the wall, and rates of heat and mass transfer within the boundary layer for a given geometry, and hence depends on additional assumptions of somewhat more questionable validity. A simplified derivation of equations treating the "adiabatic saturation" case was presented in the Second Quarterly Report², and will be reviewed here.

Under the assumptions of unity Lewis and Prandtl numbers, as considered by Denison^{10,11} and by Bartlett¹², and under certain other conditions, including equilibrium at the wall with blowing and net heat flow neglected, the wall temperature in an

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adiabatic equilibrium flow system at constant pressure becomes equal to a temperature commonly designated as the "adiabatic saturation" temperature, and defined by an enthalpy balance between free stream (stagnation) gas, virgin wall material, and saturated mixture adjacent to the wall. Depending on the heat effect of the reaction involved, be it oxidation or simple "vaporization", the adiabatic saturation temperature may be either higher or lower than that corresponding to free stream stagnation. The balance to determine the adiabatic wall conditions may be written as follows:

$$(1 + B)h_{sw} = h_{se} + Bh_w \quad (1)$$

in which

B = adiabatic saturation number, gms wall material to saturate one gm of free stream gas at T_{sw} , the saturated wall temperature.

h_{sw} = enthalpy of saturated mixture at T_{sw} , kcal/100 gms.

h_{se} = enthalpy of free stream gas at T_{se} , the stagnation temperature, kcal/100 gms.

h_w = enthalpy of virgin wall material at the temperature, T_w , at which it is added to the system, kcal/100 gms.

2.1.3 ACTUAL RATES OF EROSION

Whereas the determination of the adiabatic saturation condition from equation (1) depends only on relative rates of heat transfer versus mass transfer, absolute transport rates must be estimated in order to predict an actual rate of surface erosion. Again considering the assumptions of unit Lewis and Prandtl numbers in the manner of Denison^{10,11}, it was shown*in the Second Quarterly Report² that the overall erosion rate at steady state should be proportional, for gaseous reactants, to the adiabatic saturation number "B":

$$\dot{m} = \left(\frac{h}{C_p}\right)B \quad (2)$$

*The model described here, and designated as the "simplified Denison" approach should not be confused with the much more general case originally developed by Denison.

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in which

\dot{m} = erosion rate, lb/hr-ft².

h_c = overall heat transfer coefficient, Btu/hr-ft²-°F.

C_p = gas heat capacity, Btu/lb-°F.

The linear regression rate " \dot{r} " then follows directly:

$$\dot{r} = \left(\frac{h_c}{C_p}\right)\left(\frac{B}{\rho_w}\right) \quad (3)$$

in which

\dot{r} = regression rate, ft/hr.

ρ_w = density of wall material, lb/ft³.

In a situation with net heat flow into the refractory wall, the balance represented by equation (1) would no longer hold true. Nevertheless, it can be shown that equations (2) and (3) should still apply, provided that "B" is understood in this case to be merely the saturation number at some wall temperature T_{sw} , which must be known before the erosion rate can be estimated. This approach was adopted in comparing predicted versus measured erosion rates in the Fifth Quarterly Report⁵ under this contract.

Assuming the approximate validity of equations (2) and (3) for Lewis numbers near unity, perhaps the only remaining controversial aspect of calculations to predict erosion rates lies in the definitions of " h_c " and " C_p ", or more precisely, of their ratio $\left(\frac{h_c}{C_p}\right)$. For non-dissociating, non-reacting systems, the overall heat transfer coefficient " h_c " is unambiguous in meaning, and may be estimated using, for example, the Bartz¹³ equation for rocket nozzle heat transfer. For the dissociating case, the approach taken here in rough calculations has been to assume that both " h_c " and " C_p " increase in about the same ratio, so that the enthalpy heat transfer coefficient $\left(\frac{h_c}{C_p}\right)$ may still be estimated from standard correlations. While more sophisticated heat transfer analyses are available, their use with the simple equilibrium saturation model has not been considered justified in view of other approximations required.

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Aside from the question of attainment of equilibrium itself, the assumption of unity Lewis numbers in deriving equations (1), (2) and (3) has been considered the most likely source of error. A preliminary and elementary treatment, applying corrections to these equations for blowing, heat flow into the wall, and non-unity Lewis numbers has been under development⁵, but has not been tested against experimental data. In view of the uncertainties present in this model, it is not presented here.

In the Second Quarterly Report² it was shown that the saturation number "B" for a combustion mixture without condensed species would be equivalent to the "blowing parameter" (B') defined by Denison¹⁰, if, in addition to unity Lewis and Prandtl numbers, the Reynolds analogy between heat and momentum transfer was assumed. In other words:

$$B \approx B' = \frac{\dot{m}}{\rho_e U_e \left(\frac{f}{2}\right)} \quad (4)$$

in which

B' = blowing parameter, dimensionless.

ρ_e = gas density at outer edge of boundary layer, lb/ft³.

U_e = gas velocity at outer edge of boundary layer, ft/hr.

f = Fanning friction factor, dimensionless.

2.2 COMPUTER PROGRAM

2.2.1 NOZZLE ABLATION PROGRAM

The computation of isothermal multicomponent equilibrium with an excess of a given condensed phase may be accomplished with a number of available programs, including the single-point option of the Aeronutronic Rocket Propellant Performance Program written for the IBM 7090 computer. More conveniently, however, a separate equilibrium program might be used which would automatically converge to a saturated composition, and then compute the value of "A", the isothermal saturation number. Such a program, known as the Nozzle Ablation Program, was written for the Aeronutronic IBM 7090 computer and was described in the First Quarterly Report¹ under

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this contract. The procedure used was simply to add 2000 gms of wall material to 100 gms of the system under consideration, and then to compute the resulting equilibrium state, assuming that saturation would be achieved.

With the advent of the adiabatic saturation model for describing steady-state chemical corrosion of rocket liner materials, the original Nozzle Ablation Program had to be rewritten to include iterative solution of the enthalpy balance represented by equation (1). As described in the Second Quarterly Report², convergence is approached by assuming trial temperatures, computing isothermal saturation conditions for each temperature, and then changing temperature based on the difference between right and left hand sides of equation (1). The program was also modified to add 200, then 400, then 800, and finally 1600 gms of wall material to 100 gms system until arriving at isothermal saturation, in order to avoid the large excess of refractory phase often present in the final system if a fixed addition ratio of 20:1 was used.

The program as presently written has several options with regard to choice of free stream or saturated wall temperatures. For a real propellant system with overall heat of formation and throat pressure known in advance, the Nozzle Ablation Program can compute the throat stagnation condition in exactly the same way that a chamber condition is computed by the Rocket Propellant Performance Program, and then can calculate both isothermal and adiabatic saturation numbers for that "free stream" temperature. In the option normally used in calculations for atmospheres of arbitrary composition under this contract, however, free stream temperatures in 500°K increments from 1500°K up to 5000°K are assumed, and then both an isothermal "A" and an adiabatic "B" are computed for each such temperature. (The computations thus are arbitrarily extended without modification to temperatures above the melting point of the refractory in question.) Two options also are available for choosing the initial wall temperature " T_w " used to define " h_w ", the wall material enthalpy entering into equation (1): (a) $T_w = 298^\circ\text{K}$, (b) $T_w = T_{sw}$, the adiabatic saturated

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wall temperature. As a possibly more realistic, and certainly more severe assumption, the second case has been adopted in all calculations reported under this contract.

The usual assumptions common to most thermochemical equilibrium programs, i.e., ideal behavior in the gas phase and no solid or liquid solutions formed between condensed phases, also have been incorporated into the Nozzle Ablation Program. As a result, the program will not converge satisfactorily for systems, particularly occurring with condensed reactants, which form only condensed products at the pressure under consideration. In some cases this difficulty can be avoided by the inclusion in the input of small amounts of some inert gas such as argon, but even then, if species derived from the wall material are not present in the gas phase at equilibrium in significant amounts, convergence will not be achieved. Such cases normally indicate stoichiometric reactions which can be best treated by simple hand calculations.

2.2.2 ESTIMATION METHOD

In order to permit convenient estimation of saturation numbers for refractories exposed to complex combustion systems, a method was desired by which these numbers might be derived empirically from the saturation numbers determined under this contract for individual "pure" species, without need to perform separate computer calculations for each new case. Such a method, based upon the concept of "additivities", was investigated in the Fourth Quarterly Report⁴. It was shown that the isothermal saturation numbers "A" were additive on a weight basis for those corrosion reactions which (a) involved no net change in gaseous moles, (b) consisted of simple vaporization/decomposition of the refractory, or (c) went to stoichiometric completion. For individual reactions involving either a net increase or a net decrease in gaseous moles, moreover, algebraic equations could be derived which corrected for the effects of pressure and dilution, yielding "blending" saturation numbers which also were additive.

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The analysis did not extend to the prediction of adiabatic saturation numbers, but was concerned only with the isothermal "A's".

In testing the estimation method for true propellant systems, it was found, however, that interactions occurred in many situations of interest, such that any prediction based upon additivities would necessarily fail. Such an interaction could lead either to a decrease in saturation number for the mixture, or, alternatively, to an increase. As an example of the former, attempts to combine saturation numbers for graphite + H_2 and graphite + F_2 would overpredict the corrosivity of a nominal mixture of H_2 + F_2 at the same temperature, owing to failure to take into account the stability of the gaseous HF molecule. As an example of the latter⁴, combining the saturation numbers for graphite + H_2 and graphite + N_2 tends to underpredict the corrosivity of a mixture containing H_2 + N_2 , since gaseous HCN becomes a major reaction product of graphite with the mixture. Therefore, the estimation method has been deemed generally unsatisfactory for predicting theoretical corrosion with real propellant systems.

2.3 THERMODYNAMIC DATA

The thermodynamic data for combustion species used in equilibrium computations under this contract were taken, wherever available, from the JANAF tables¹⁴. In certain cases, particularly for condensed species, the JANAF data did not cover the entire range from 298°K up to 6000°K. In such instances, the JANAF data usually were extended, using best estimates of heat capacities, and, where applicable, heats of fusion and melting points. In a few cases, where the species involved was known to become increasingly unstable at higher temperatures, the data were truncated rather than extrapolated, so that the species would not be considered above a certain temperature.

For several heavy metal compounds considered as refractories, the pertinent species families either were not adequately covered in the JANAF tables, or, in a few cases, were not even given at all (Ex. - Ta, Hf, Mo, Nb, Th). Thus, a significant portion of the effort under this contract

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was devoted to compiling the thermodynamic data necessary to consider some of these chemical systems. Where available, data published in sources aside from JANAF were selected, but in most cases estimation was required, using methods standard throughout the literature. Compilations of such data were given in the First¹, Second² and Third³ Quarterly Reports. In order to make these data more easily retrievable, however, the thermodynamic properties of 57 species of Ta, W and Hf not contained in the JANAF tables have been reprinted as Volume II of this report.

In addition to those species listed in Volume II, the thermodynamic data previously estimated for $WCl_5(g)$, $WCl_6(g)$, $WF(g)$, and $ZrB_2(c)$ have recently been superseded by new JANAF data¹⁵. The thermodynamic properties of condensed $HfCl_2(c)$, $HfCl_3(c)$, $HfF_2(c)$, and $HfF_3(c)$ moreover were taken, in calculations, to be identical, except for molecular weight, to the JANAF data for the corresponding Zr species. The data for five additional species, $C_2H(g)$, $ZrOCl(g)$, $ZrOCl_2(g)$, $ZrOF(g)$, and $ZrOF_2(g)$, were previously published by Aeronutronic under another contract.^{16,17} In order that the exact thermodynamic values assumed for the chemical corrosion studies be properly available, the data for $C_2H(g)$, the three W species, and the five Zr species just cited are reprinted in the Appendix of this volume.

A listing of all pertinent species considered in the chemical corrosion studies and the propellant performance studies carried out under this contract is given in Table I. The designation "/c" after a species indicates a condensed phase, and is meant to include both liquid and solid states, where applicable. (In the JANAF tables, the liquid and solid are considered as separate species.)

TABLE I
SPECIES CONSIDERED IN EQUILIBRIUM CALCULATIONS

<u>O Species</u>	<u>F Species</u>	<u>C Species</u> (cont.)	<u>C Species</u> (cont.)
O	F	C ₅	CH ₃ F
O ₂	F ₂	CO	CH ₂ F ₂
O ₃	OF	CO ₂	CHF ₃
	HF	CH	HCOF
<u>H Species</u>	HOF	CH ₂	CNF
H	NF	CH ₃	CCl
H ₂	NF ₂	CH ₄	CCl ₄
OH	NOF	C ₂ H	COCl ₂
H ₂ O		C ₂ H ₂	CH ₃ Cl
	<u>Cl Species</u>	C ₂ H ₄	CNCI
<u>N Species</u>	Cl	CHO	CClF ₃
N	Cl ₂	CH ₂ O	CCl ₂ F ₂
N ₂	ClO	CN	COCIF
NO	HCl	C ₂ N ₂	CHClF ₂
NO ₂	HCIO	C ₄ N ₂	C/c
N ₂ O	NOC1	HCN	
NH	NO ₂ Cl	HCNO	<u>B Species</u>
NH ₂	ClF	CF	B
NH ₃		CF ₂	BO
NOH	<u>C Species</u>	CF ₃	BO ₂
	C	CF ₄	B ₂ O ₂
	C ₂	C ₂ F ₂	B ₂ O ₃
	C ₃	C ₂ F ₄	BH
	C ₄	COF ₂	BH ₂

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TABLE I (continued)

SPECIES CONSIDERED IN EQUILIBRIUM CALCULATIONS

<u>B Species</u> (cont.)	<u>Al Species</u>	<u>Li Species</u>	<u>Li Species</u> (cont.)
BH ₃	Al	Li	LiBO ₂ /c
HBO	AlO	Li ₂	Li ₂ B ₄ O ₇ /c
HBO ₂	Al ₂ O	LiO	Li ₂ B ₆ O ₁₀ /c
H ₂ BO ₂	Al ₂ O ₂	Li ₂ O	Li ₂ B ₈ O ₁₃ /c
H ₃ BO ₃	AlH	LiH	LiAlO ₂ /c
BF	AlOH	LiOH	
BF ₂	HAIO ₂	(LiOH) ₂	<u>Be Species</u>
BF ₃	AlN	LiN	Be
BOF	AlF	LiF	BeO
(BOF) ₃	AlF ₂	(LiF) ₂	(BeO) ₂
HBOF ₂	AlF ₃	(LiF) ₃	(BeO) ₃
BCl	AlOF	LiOF	(BeO) ₄
BCl ₂	AlCl	LiCl	(BeO) ₅
BCl ₃	AlCl ₂	(LiCl) ₂	(BeO) ₆
BOCl	AlCl ₃	LiClO	BeH
(BOCl) ₃	AlOCl	Li ₂ ClF	BeH ₂
BClF	AlClF	LiBO ₂	BeOH
BClF ₂	AlClF ₂	LiAlF ₄	Be(OH) ₂
BCl ₂ F	AlCl ₂ F	Li/c	BeF
B ₂ Cl ₄	Al/c	Li ₂ O/c	BeF ₂
BC	Al ₂ O ₃ /c	LiH/c	BeCl
B/c	AlN/c	LiOH/c	BeCl ₂
B ₂ O ₃ /c	AlF ₃ /c	Li ₃ N/c	BeClF
HBO ₂ /c	AlCl ₃ /c	LiF/c	BeC ₂
H ₃ BO ₃ /c	Al ₄ C ₃ /c	LiCl/c	BeB ₂ O ₄
BN/c		Li ₂ C ₂ /c	
(BOF) ₃ /c			
B ₄ C/c			

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TABLE I (continued)

SPECIES CONSIDERED IN EQUILIBRIUM CALCULATIONS

<u>Be Species</u> (cont.)	<u>Mg Species</u> (cont.)	<u>Ta Species</u> (cont.)	<u>Ti Species</u> (cont.)
LiBeF ₃	MgF ₂ /c	TaOCl ₃	Ti ₂ O ₃ /c
Be/c	MgCl ₂ /c	TaO ₂ Cl	Ti ₃ O ₅ /c
BeO/c	MgC ₂ /c	Ta/c	TiN/c
Be(OH) ₂ /c	Mg ₂ C ₃ /c	Ta ₂ O ₅ /c	TiF ₂ /c
Be ₃ N ₂ /c	Al ₂ MgO ₄ /c	TaN/c	TiF ₃ /c
BeF ₂ /c		TaCl ₃ /c	TiF ₄ /c
BeCl ₂ /c	<u>Ta Species</u>	TaCl ₄ /c	TiCl ₂ /c
Be ₂ C/c	Ta	TaCl ₅ /c	TiCl ₃ /c
Al ₂ BeO ₄ /c	TaO	TaC/c	TiC/c
	TaO ₂	TaB ₂ /c	TiB ₂ /c
<u>Mg Species</u>	TaF		Li ₂ TiO ₃ /c
Mg	TaF ₂	<u>Ti Species</u>	MgTiO ₃ /c
MgO	TaF ₃	Ti	MgTi ₂ O ₅ /c
MgH	TaF ₄	TiO	Mg ₂ TiO ₄ /c
MgOH	TaF ₅	TiO ₂	
MgF	TaOF	TiF	<u>Zr Species</u>
MgF ₂	TaOF ₂	TiF ₂	Zr
MgCl	TaOF ₃	TiF ₃	ZrO
MgCl ₂	TaO ₂ F	TiF ₄	ZrO ₂
MgClF	TaCl	TiCl	ZrF
Mg/c	TaCl ₂	TiCl ₂	ZrF ₂
MgO/c	TaCl ₃	TiCl ₃	ZrF ₃
MgH ₂ /c	TaCl ₄	TiCl ₄	ZrF ₄
Mg(OH) ₂ /c	TaCl ₅	Ti/c	ZrOF
Mg ₃ N ₂ /c	TaOCl	TiO/c	ZrOF ₂
	TaOCl ₂	TiO ₂ /c	ZrCl

TABLE I (continued)
SPECIES CONSIDERED IN EQUILIBRIUM CALCULATIONS

<u>Zr Species</u> (cont.)	<u>W Species</u> (cont.)	<u>W Species</u> (cont.)	<u>Hf Species</u> (cont.)
ZrCl ₂	H ₂ WO ₄	WCl ₄ /c	Hf/c
ZrCl ₃	WF	WCl ₅ /c	HfO ₂ /c
ZrCl ₄	WF ₂	WCl ₆ /c	HfN/c
ZrOCl	WF ₄	WOCl ₄ /c	HfF ₂ /c
ZrOCl ₂	WF ₅	WO ₂ Cl ₂ /c	HfF ₃ /c
Zr/c	WF ₆	WC/c	HfF ₄ /c
ZrO ₂ /c	WOF ₂	WB/c	HfCl ₂ /c
ZrN/c	WOF ₄		HfCl ₃ /c
ZrF ₂ /c	WO ₂ F ₂	<u>Hf Species</u>	HfCl ₄ /c
ZrF ₃ /c	WCl	Hf	HfC/c
ZrF ₄ /c	WCl ₂	HfO	HfB ₂ /c
ZrCl ₂ /c	WCl ₄	HfO ₂	
ZrCl ₃ /c	WCl ₅	HfF	<u>Rare Gas Species</u>
ZrCl ₄ /c	WCl ₆	HfF ₂	He
ZrC/c	WOCl ₂	HfF ₃	Ar
ZrB ₂ /c	WOCl ₄	HfF ₄	Kr
	WO ₂ Cl ₂	HfOF	
<u>W Species</u>	W/c	HfOF ₂	
W	WO ₂ /c	HfCl	
WO	WO ₃ /c	HfCl ₂	
WO ₂	H ₂ WO ₄ /c	HfCl ₃	
WO ₃	WF ₆ /c	HfCl ₄	
(WO ₃) ₃	WOF ₄ /c	HfOCl	
(WO ₃) ₄	WCl ₂ /c	HfOCl ₂	

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2.4 SYSTEMS INVESTIGATED

The refractory materials studied during this program were selected from an original list including the following¹⁸:

<u>Metals:</u>	C, W, Ta, Mo
<u>Carbides:</u>	TaC, HfC, NbC, ZrC, TiC, Al ₄ C ₃ , B ₄ C, SiC
<u>Nitrides:</u>	TaN, HfN, ZrN, TiN, AlN, BN, Si ₃ N ₄
<u>Oxides:</u>	MgO, ZrO ₂ , BeO, ThO ₂
<u>Borides:</u>	HfB ₂ , ZrB ₂ , TiB ₂

Those materials actually investigated, either through rigorous machine computation or by approximate hand calculation, were as follows: C, W, TaC, HfC, ZrC, TiC, HfN, TiN, MgO, ZrO₂, ThO₂, and ZrB₂.

The major portion of the theoretical corrosion studies were carried out for "pure" combustion species, rather than for real propellant systems. The species considered included AlF₃, BF₂, BF₃, BOF, HBO₂, BeF₂, CO, CO₂, HCl, HF, H₂, H₂O, LiF, N₂, Al₂O₃/c, and BeO/c. It was recognized, however, that at the "free-stream" temperatures and pressures involved, many of these nominal species would be largely dissociated or disproportionated.

The "pure" species systems actually investigated are shown in Table II in terms of a matrix involving 9 refractories and 16 species. Except as otherwise to be noted, all calculations were for a total pressure of 1000 psia, and for temperatures in the range 1500-5000°K. The results were presented in terms of two types of plots, one type showing isothermal "A" and adiabatic "B" as functions of wall temperature and free-stream temperature, respectively, and the other type showing individual species concentrations in the saturated mixture as functions of wall temperature. The relative corrosivities versus temperature and the heat effects involved could be read from the first type of plot, while the ablation chemistry could be interpreted from the second type.

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TABLE II

CHEMICAL CORROSION OF REFRACTORY MATERIALS;
"PURE" SPECIES SYSTEMS STUDIED

	<u>C/c</u>	<u>W/c</u>	<u>TaC/c</u>	<u>HfN/c</u>	<u>TiC/c</u>	<u>ZrC/c</u>	<u>ZrB₂/c</u>	<u>MgO/c</u>	<u>HfO₂/c</u>
AlF ₃	2	3	4	5	-	-	-	-	-
BF ₂	2	3	4	5	-	-	-	-	-
BF ₃	2	3	4	5	-	-	-	-	-
BOF	2	3,4	4	5	-	-	-	-	-
HBO ₂	2	(3)	(4)	-	-	-	-	-	-
BeF ₂	2,6	3,6	4,6	5	-	-	-	-	-
CO	1,2	3,4	4	5	2	2	2	-	-
CO ₂	1,2	3,4	4	5	2	2	2	4	4
HCl	1,2	3	4	5	2	2	2	-	-
HF	1,2	3	4	5	2	2	2	-	-
H ₂	1,2	6	4	5	2	2	2	-	-
H ₂ O	1,2	6	4	5	2	2	2	-	-
LiF	2	3	4	5	-	-	-	-	-
N ₂	1,2	6	4	5	2,4	2,4	2	-	-
Al ₂ O ₃ /c	2,5	5	5	5	-	-	-	-	-
BeO/c	2	-	-	-	-	-	-	-	-

KEY: 1 - First QPR, 9/15/62¹ 4 - Fourth QPR, 6/15/63⁴
 2 - Second QPR, 12/15/62² 5 - Fifth QPR, 9/15/63⁵
 3 - Third QPR, 3/15/63³ 6 - Final Report, 12/15/63

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As may be seen from Table II, graphite was considered with seven non-metallized species in the First¹ and Second² Quarterly Reports, and with the remaining metallic species also in the Second Quarterly. The calculations presented in the First Quarterly Report covered only the isothermal saturation case, while in the Second Quarterly, both isothermal and adiabatic saturation parameters were included. Also shown in the Second Quarterly were the effects of total pressure on theoretical corrosion parameters for graphite exposed to H_2 , H_2O and CO_2 . Only in the case of the $C/c + H_2$ reaction was there an appreciable net change in gaseous moles, and hence, a significant pressure effect.

Theoretical corrosion studies for tungsten attacked by 11 common combustion species were presented in the Third Quarterly Report³. The calculations for W/c and BOF , CO , and CO_2 were revised in the Fourth Quarterly Report⁴, based upon new JANAF¹⁹ data for the gaseous tungsten oxides. The $W/c + H_2O$ case was again deferred, however, pending adoption of JANAF tables for gaseous and condensed H_2WO_4 . It is also interesting to note that whereas the system $C/c + HBO_2$ yielded reasonable saturation compositions over the entire temperature range², the system $W/c + HBO_2$ apparently was completely condensed except at temperatures in the vicinity of $5000^\circ K$.³ The difference resulted from the calculated high stability of the species HBO_2/c , which was added to the thermodynamic file in the interim between the two reports. In view of the considerable extrapolation involved in predicting high temperature thermodynamic values for condensed HBO_2/c , all calculations including this species are considered extremely unreliable.

The theoretical corrosion parameters for TaC/c attacked by 14 "pure" combustion species were presented in the Fourth Quarterly Report⁴, and corresponding results for HfN/c considered as a possible refractory were given in the Fifth Quarterly Report⁵. Again, the system $TaC/c + HBO_2$ was found to give a rather meaningless result, and was not reported in detail. Also for this reason, HBO_2 as a "pure" species was not even calculated with HfN/c as an ablator.

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The three refractories TiC/c, ZrC/c, and ZrB₂/c were considered only with the seven non-metallized species CO, CO₂, HCl, HF, H₂, H₂O, and N₂. These data all were presented in the Second Quarterly Report². In the Fourth Quarterly Report⁴, the refractory oxides were considered briefly for application in a CO₂ atmosphere. Rigorous theoretical corrosion calculations were performed for MgO/c and HfO₂/c, while rough hand calculations were made for ThO₂/c, the highest-melting oxide.

Besides the normal chemical corrosion calculations for 1000 psia total pressure, certain special cases also were considered. In the Fourth Quarterly Report⁴, hand calculations were employed in comparing the relative stabilities of TaC/c, TiC/c, and ZrC/c in N₂ atmospheres, in other words, in estimating the partial pressures of N₂ in equilibrium simultaneously with the metal carbide, metal nitride, and graphite. In the Fifth Quarterly Report⁵, the results of machine computations were given for the theoretical corrosion of C/c, W/c, TaC/c, and HfN/c by condensed Al₂O₃/c, under conditions such that both condensed phases would be present at equilibrium. The true total pressure, then, would vary with temperature in much the manner of a "mixed vapor pressure". The single-point feature of the Rocket Propellant Performance Program was used for these calculations, with argon added to yield a nominal total pressure.

Inasmuch as revised JANAF data for gaseous and condensed H₂WO₄ have recently been received²⁰, the W/c + H₂O system was computed for inclusion in this report. The two systems W/c + H₂ and W/c + N₂, originally excluded owing to their expected non-reactivity, also were treated, but only by simple hand calculation, in order to show the effect of tungsten volatility. The species concentration plots for these three cases are presented in Figure 1, in which \bar{x} (moles of gas per 100 grams system) and condensed species concentrations (moles per 100 grams system) are shown according to the practice first adopted in the Third Quarterly Report³. The "A" and "B" saturation parameters for W/c and H₂, H₂O, and N₂ are presented (in terms of $\frac{B}{P}$) as part of Figures 12, 13, and 15, respectively.

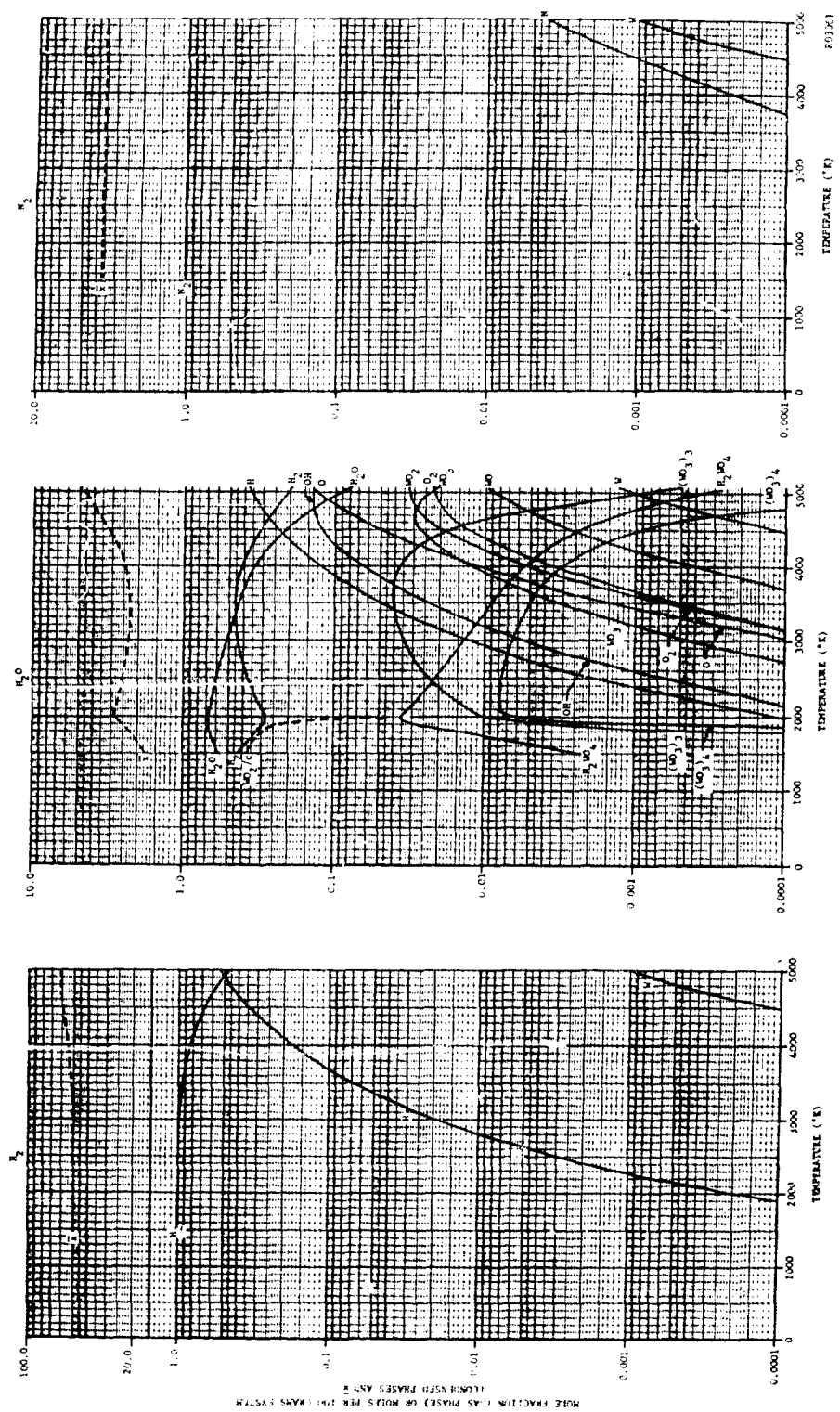


FIGURE 1. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT 1000 PSIA FOR W/c EXPOSED TO H_2 , H_2O , AND N_2 .

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As a result of a recent drastic revision in the JANAF¹⁹ heat of formation for gaseous BeF, the theoretical corrosion calculations previously performed for C/c, W/c, and TaC/c (but not HfN/c) exposed to BeF₂ were invalidated, and also had to be repeated. In Figure 2 are shown the new composition plots for these three refractories attacked by BeF₂; the new "A" and "B" values (divided by densities) are indicated in Figure 7. The effect of the change in thermodynamic properties for BeF is to make a BeF₂ atmosphere much less corrosive than was formerly believed.

A limited number of real propellant systems were investigated for chemical corrosion effects in the course of this program. In Section 3 of the Fifth Quarterly Report⁵, saturation numbers were given for graphite attacked by Arcite 368, Arcite 373, "NP", and "NF" propellants. Calculations also have been made for W/c and TaC/c with the "NF" propellant, and for various refractories exposed to F₂/H₂ (fuel-rich), "hot solid", and "BOF simulation" mixtures. The theoretical corrosion parameters for these latter systems are given in Figures 17 through 21 of this report.

In the section to follow, refractory materials are rated by their comparative resistance to various corrosive atmospheres. This presentation is exactly the opposite of that previously followed in the Quarterlies, in which different "pure" species were compared, at least indirectly, for each separate refractory substance considered. All systems not falling into a comparison on this new basis have been excluded from further discussion in this report.

SECTION 3

THEORETICAL RATING OF MATERIALS

3.1 THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO VARIOUS
"PURE" PROPELLANT SPECIES

The theoretical corrosion parameters determined under this contract for refractory materials exposed to various "pure" propellant species have been correlated in terms of relative ratings of materials with a given species. The nominal species considered have included AlF_3 , BF_2 , BF_3 , BOF , BeF_2 , CO , CO_2 , HCl , HF , H_2 , H_2O , LiF , N_2 , and $\text{Al}_2\text{O}_3/\text{c}$. The refractories C/c , W/c , TaC/c and HfN/c were considered with all 14 species, whereas TiC/c , ZrC/c , and ZrB_2/c were considered only with the non-metallized species, and MgO/c and HfO_2/c , only with CO_2 . All comparisons except those with $\text{Al}_2\text{O}_3/\text{c}$ are for a total pressure of 1000 psia. Graphical rating correlations for the 14 cases are shown in Figures 3 through 16, respectively.

The primary rating parameter considered has been $\frac{B}{\rho}$ (volume of refractory to saturate a unit weight of gas) as a function of wall temperature. As previously stated, under assumptions of equilibrium reaction with Lewis and Prandtl numbers equal to unity, $\frac{B}{\rho}$, for a given enthalpy heat transfer coefficient, should be directly proportional to the linear regression rate of the surface under attack. In view of the controversial aspect of calculations required to estimate over-all heat and mass transfer

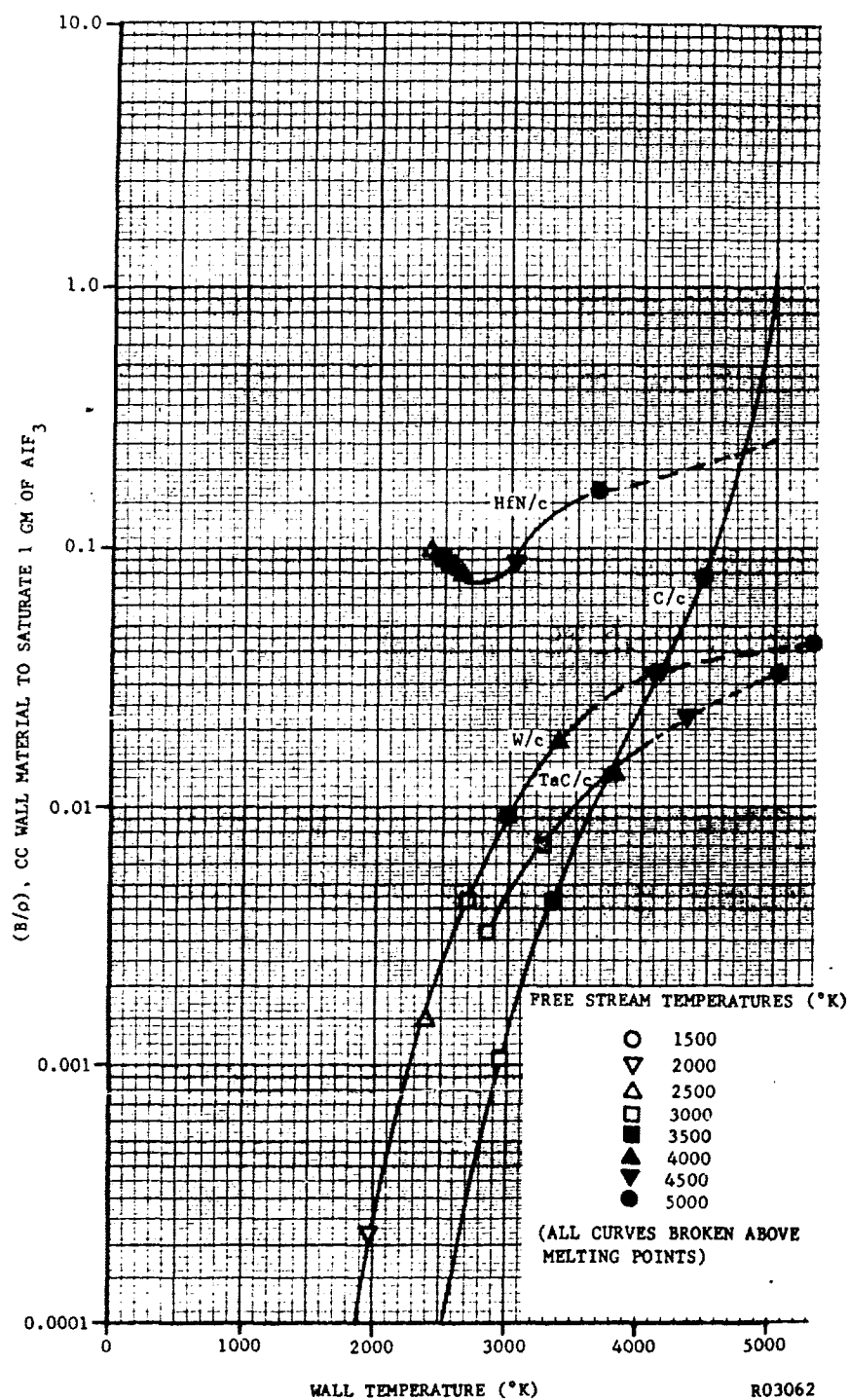
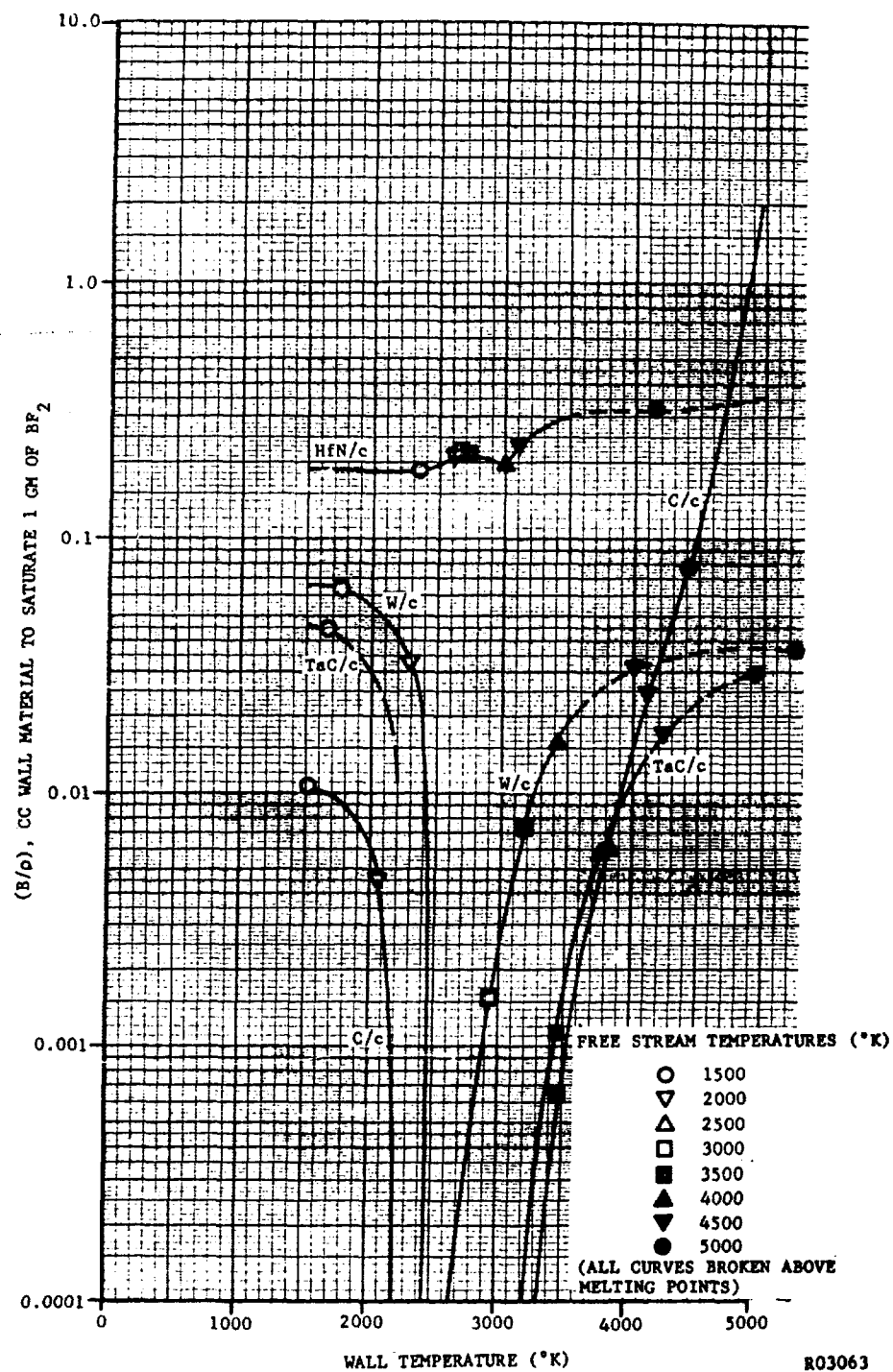


FIGURE 3. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO AlF_3 AT 1000 PSIA



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FIGURE 4. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO BF_2 AT 1000 PSIA

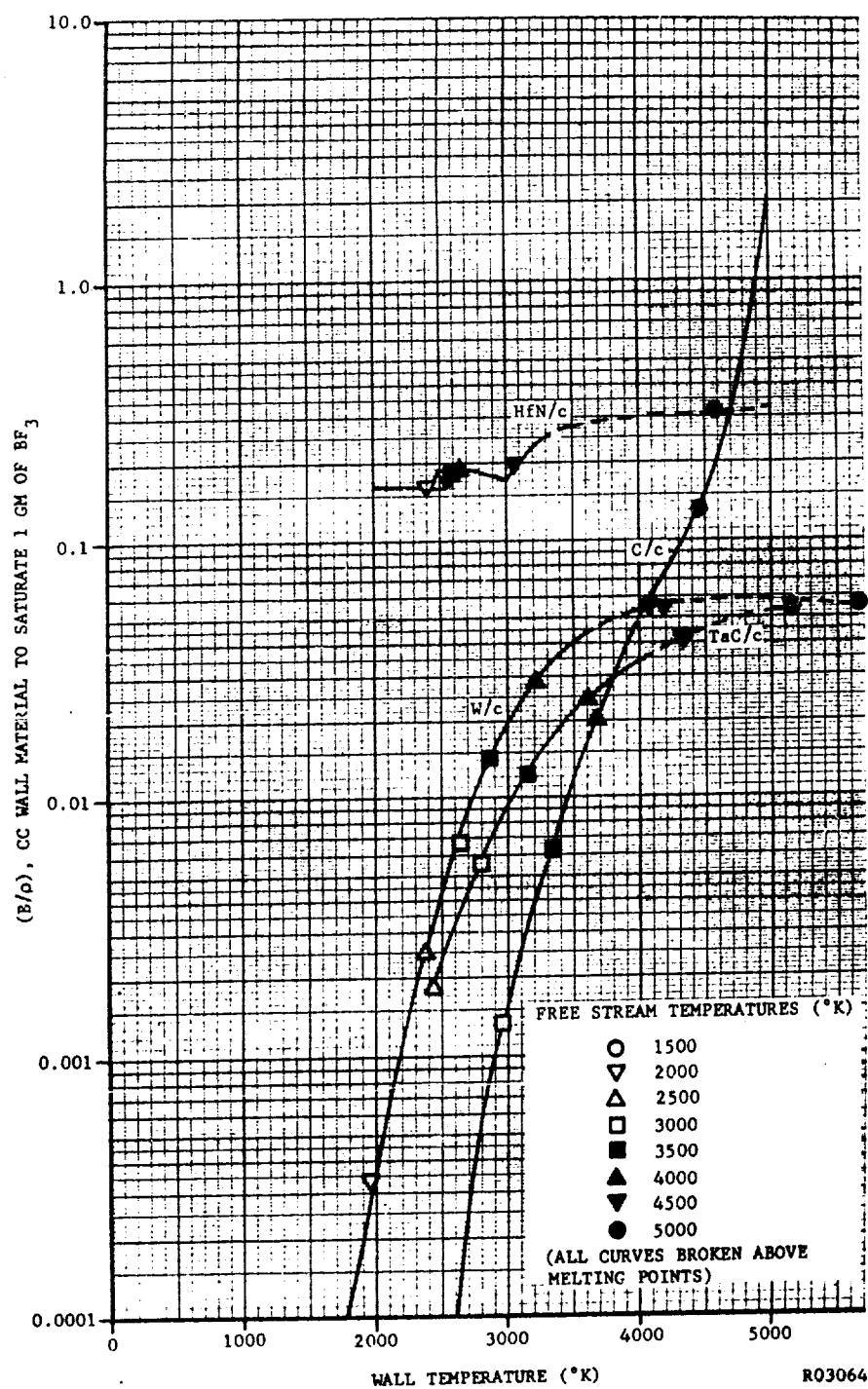


FIGURE 5. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO BF₃ AT 1000 PSIA

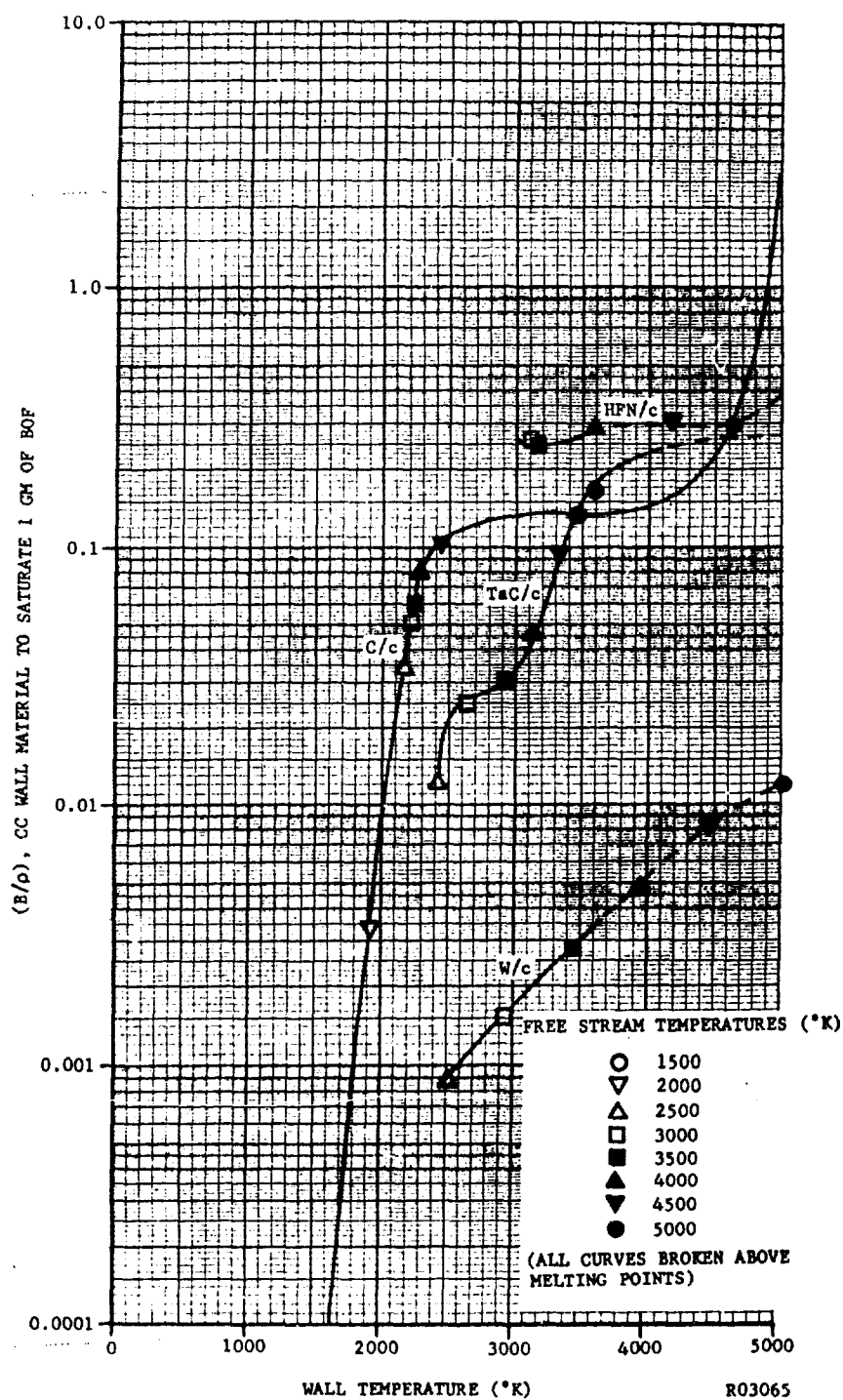
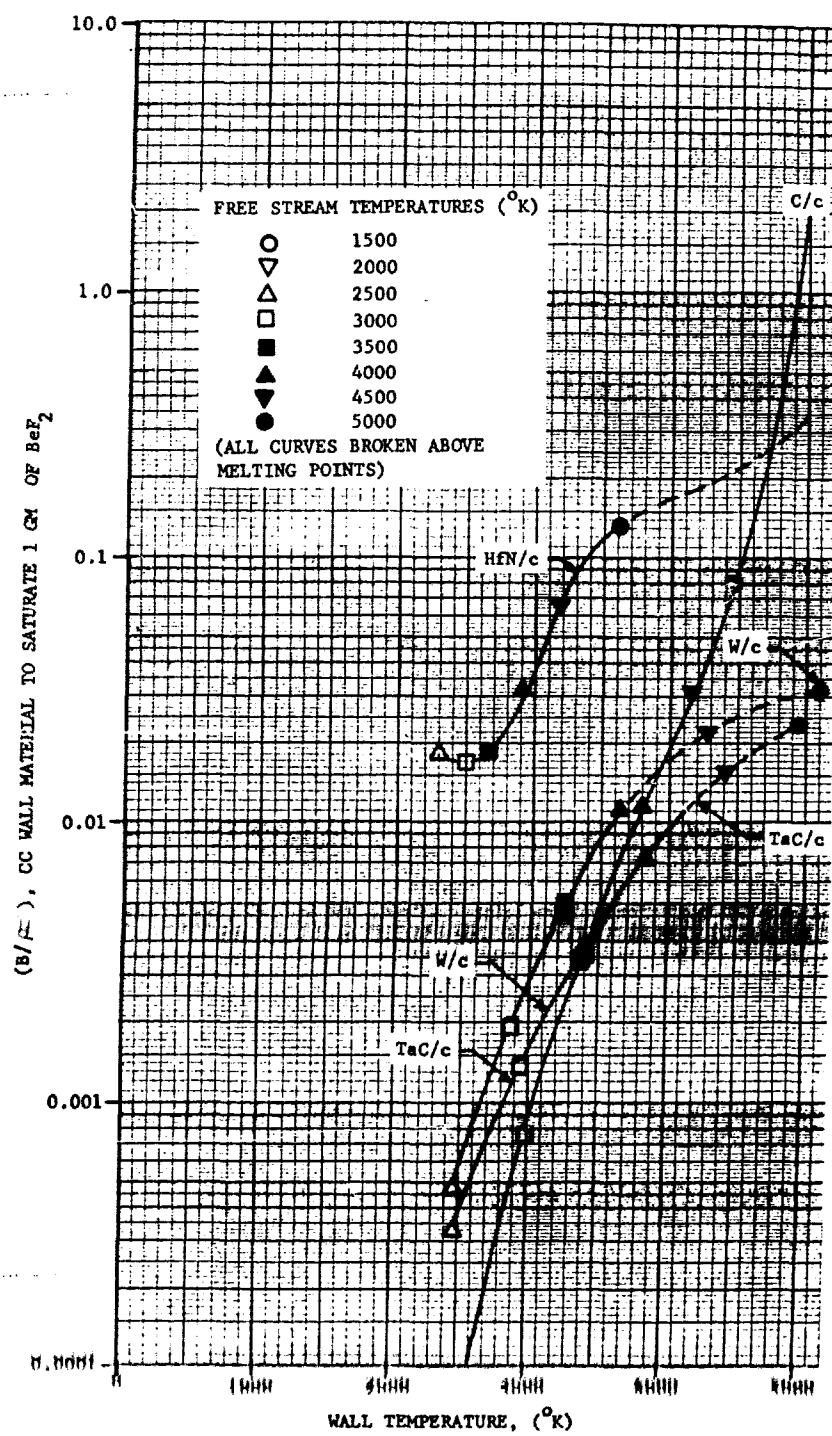


FIGURE 6. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO BOF AT 1000 PSIA



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FIGURE 7. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO BeF_2 AT 1000 PSIA

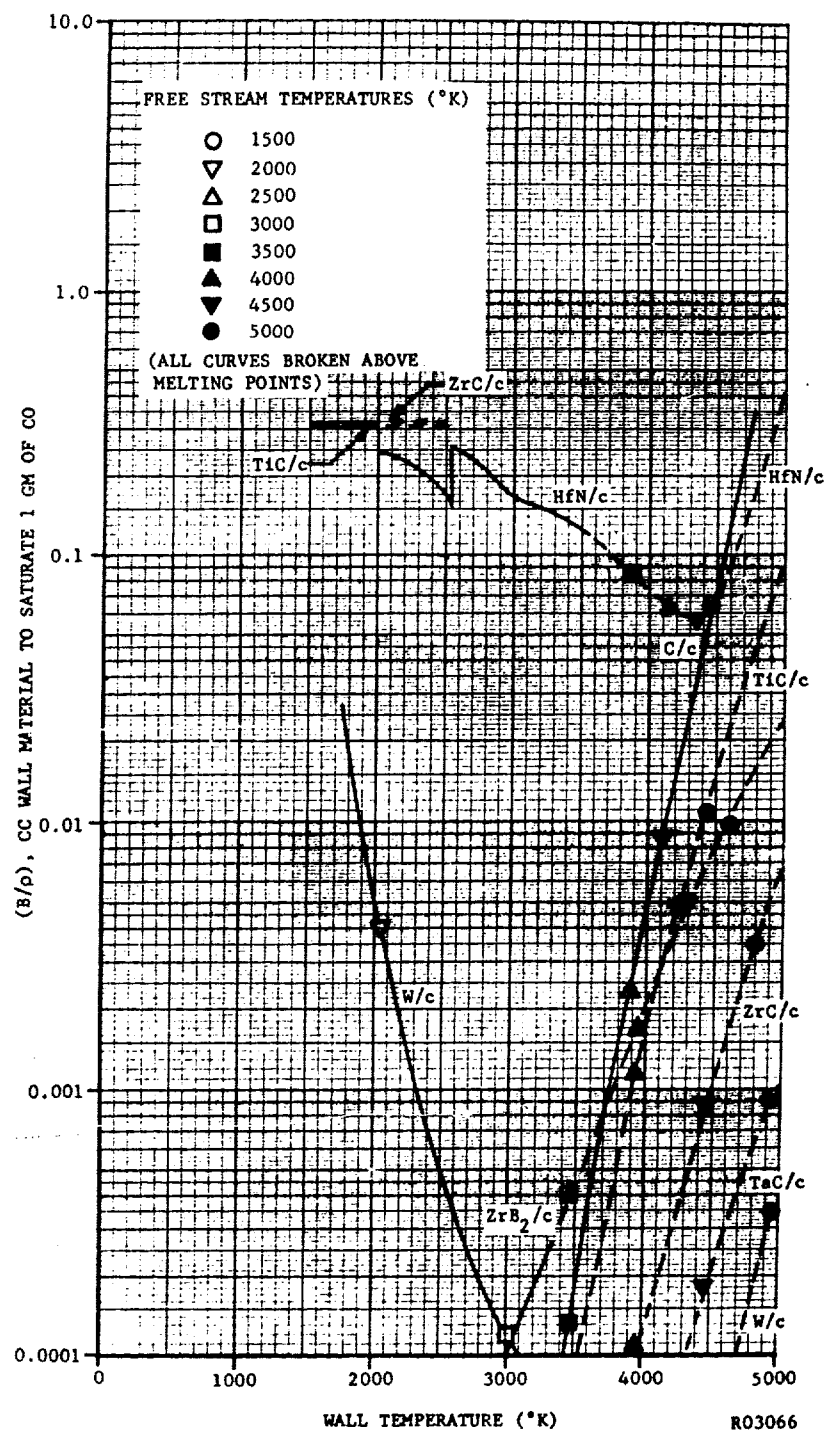


FIGURE 8. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO CO AT 1000 PSIA

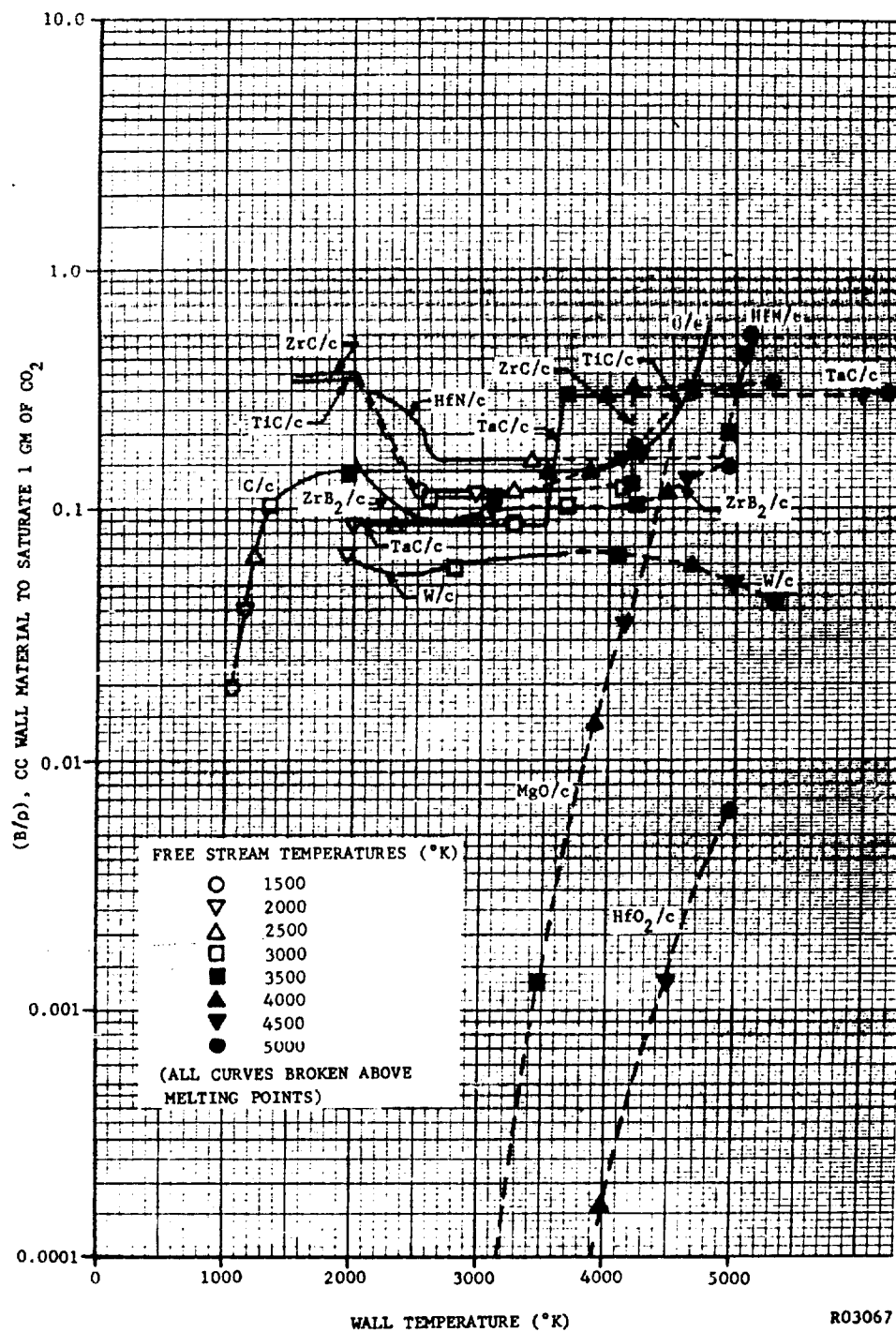


FIGURE 9. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO CO₂ AT 1000 PSIA

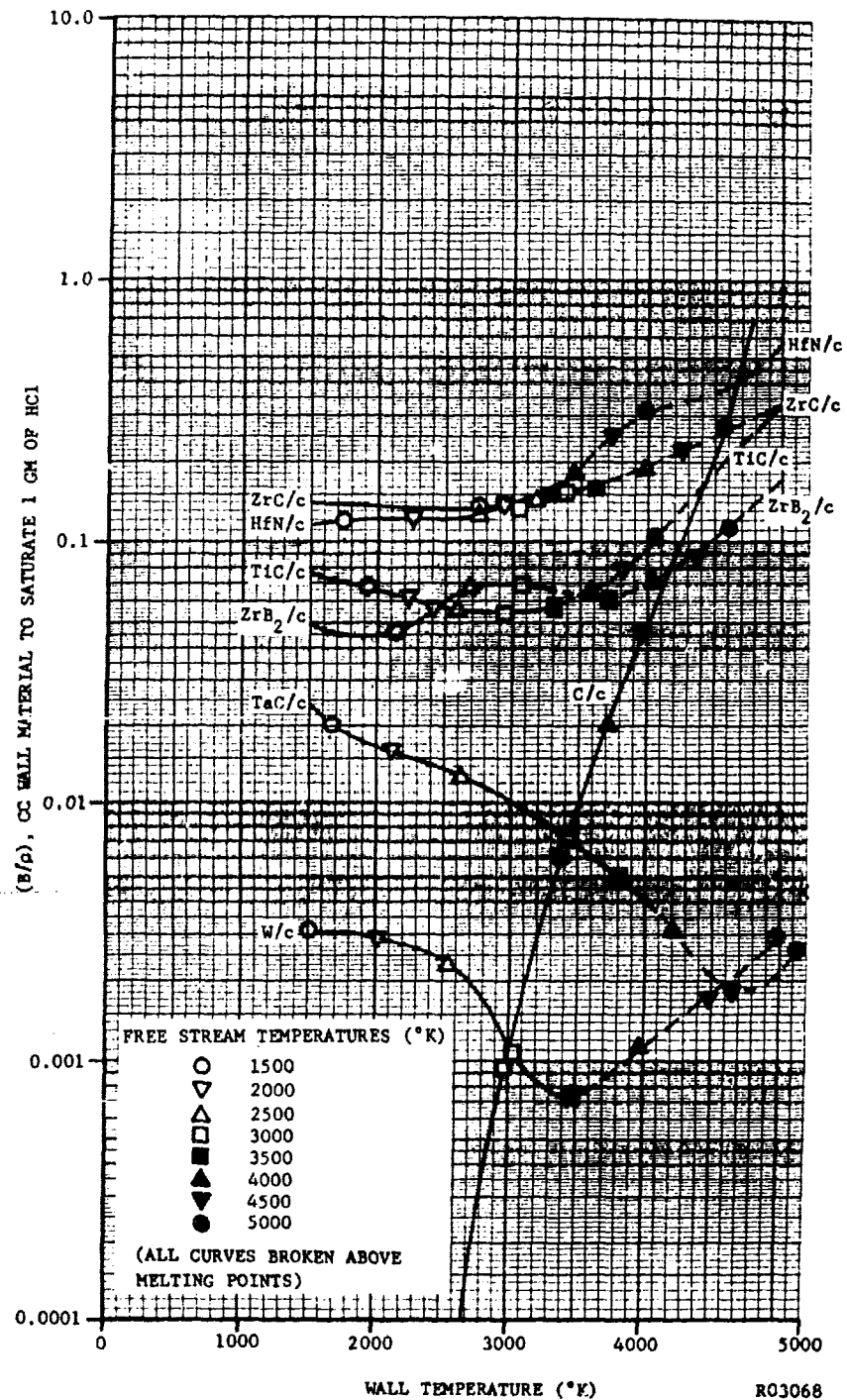


FIGURE 10. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO HCl AT 1000 PSIA

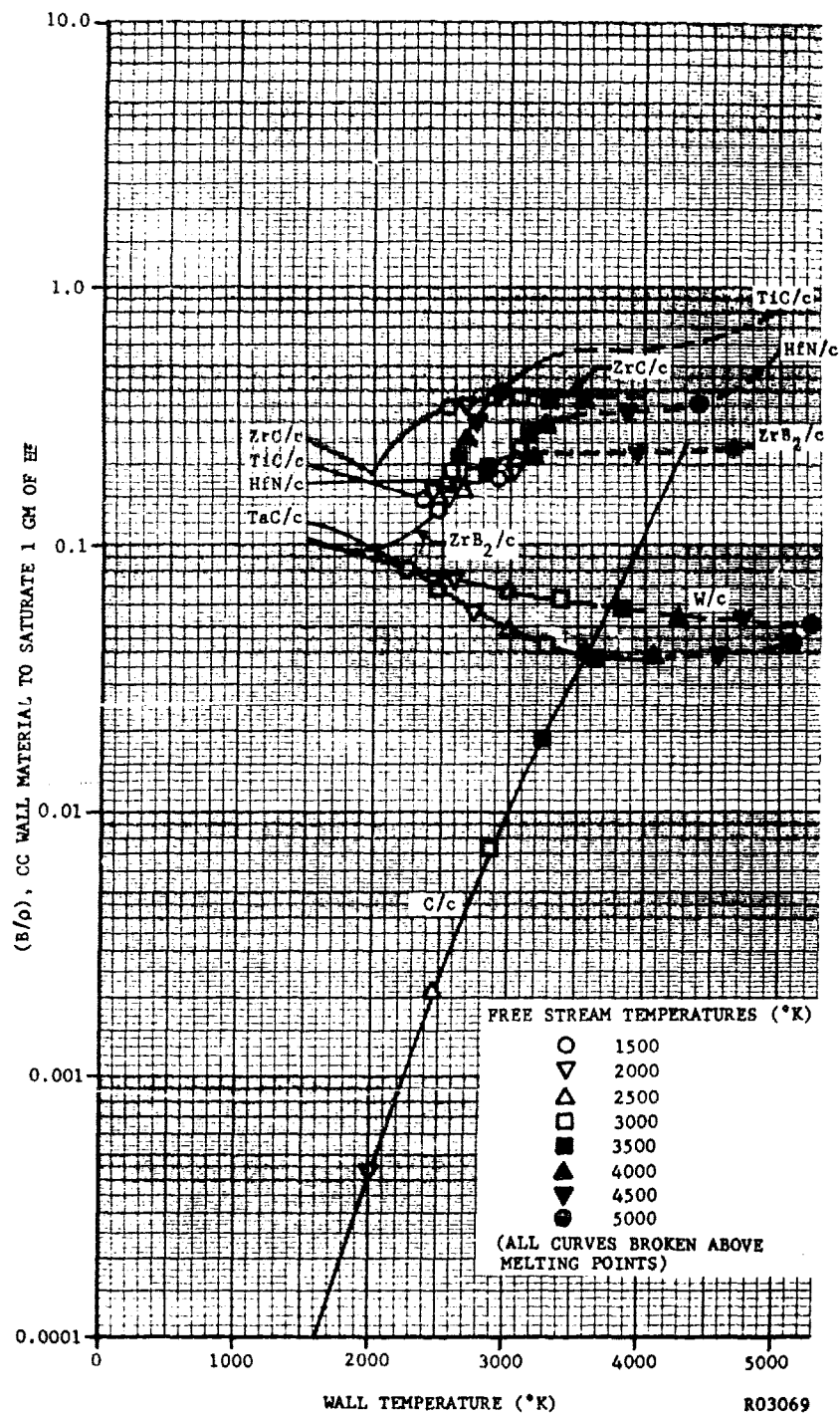


FIGURE 11. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO HF AT 1000 PSIA

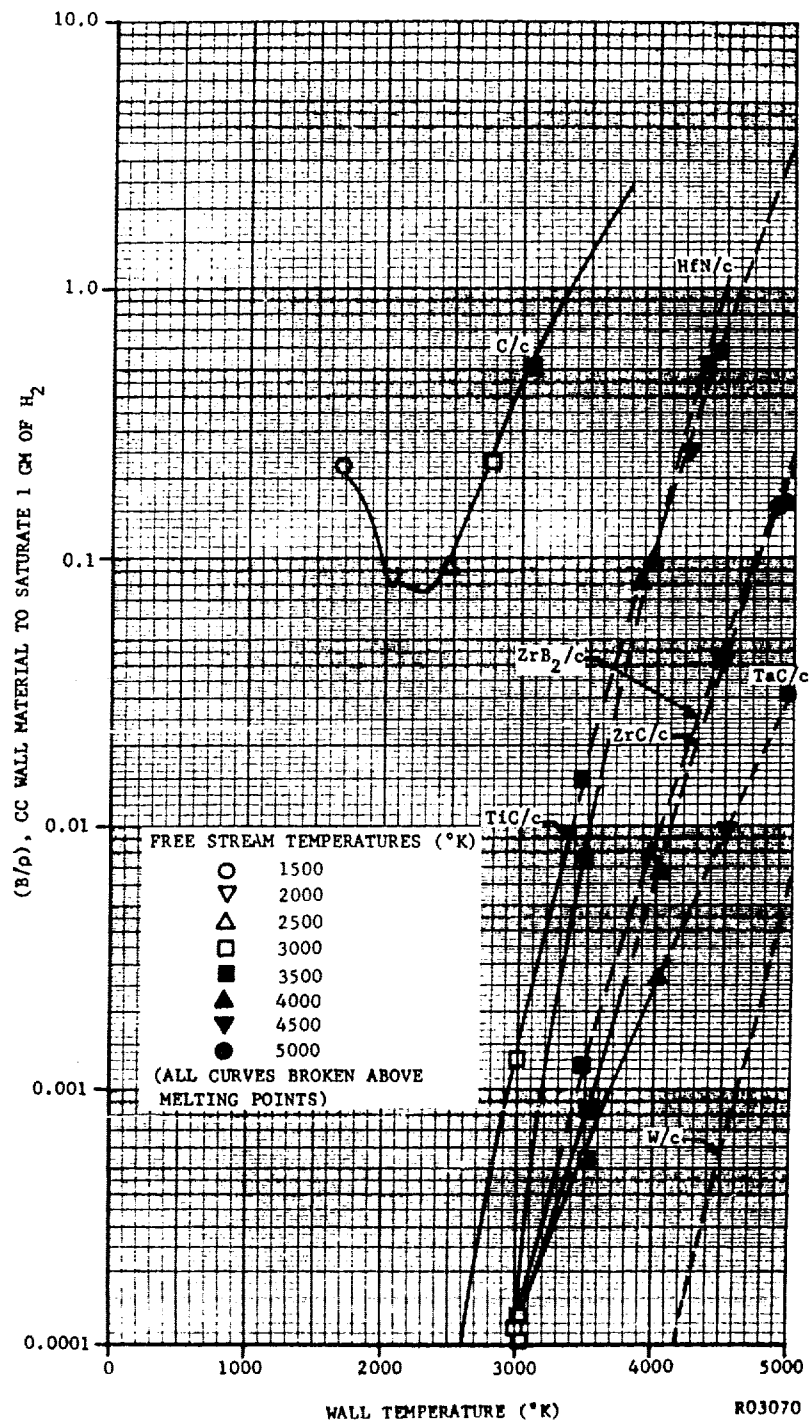


FIGURE 13. DIFFERENTIAL RATING OF REFRACTORY MATERIALS EXPOSED TO H_2 AT 1000 PSIA

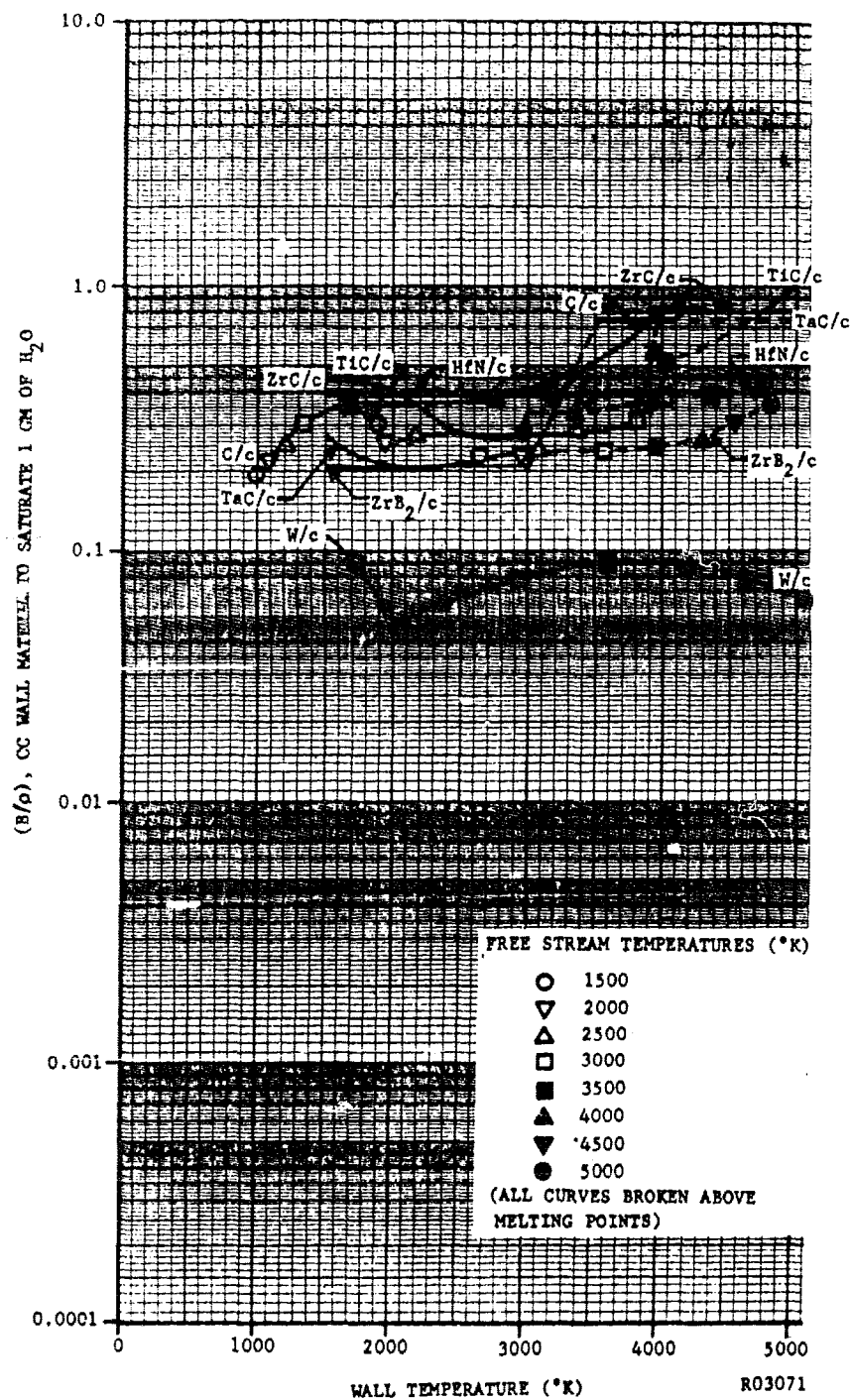


FIGURE 13. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO H₂O AT 1000 PSIA

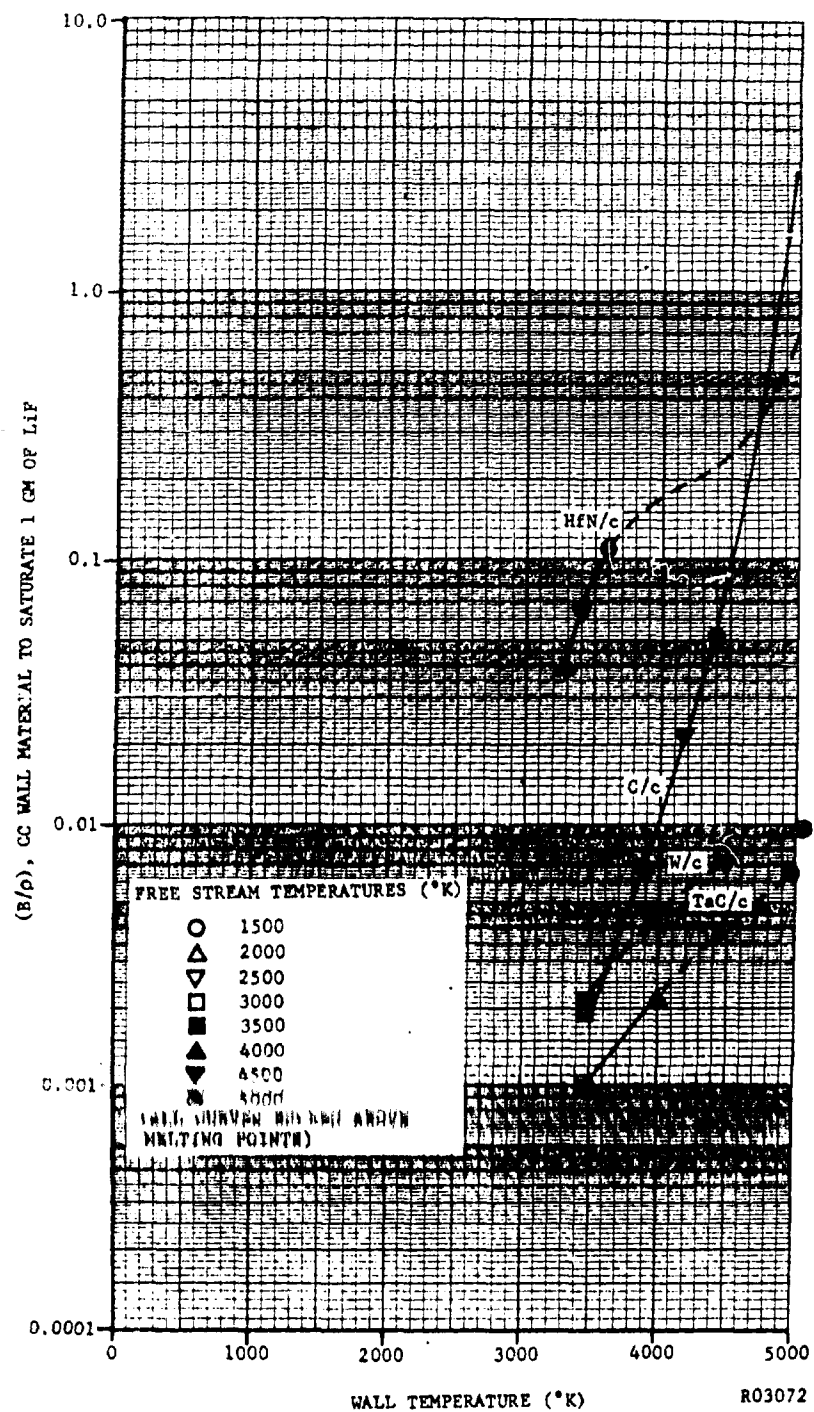


FIGURE 14. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO LiF AT 1000 PSIA

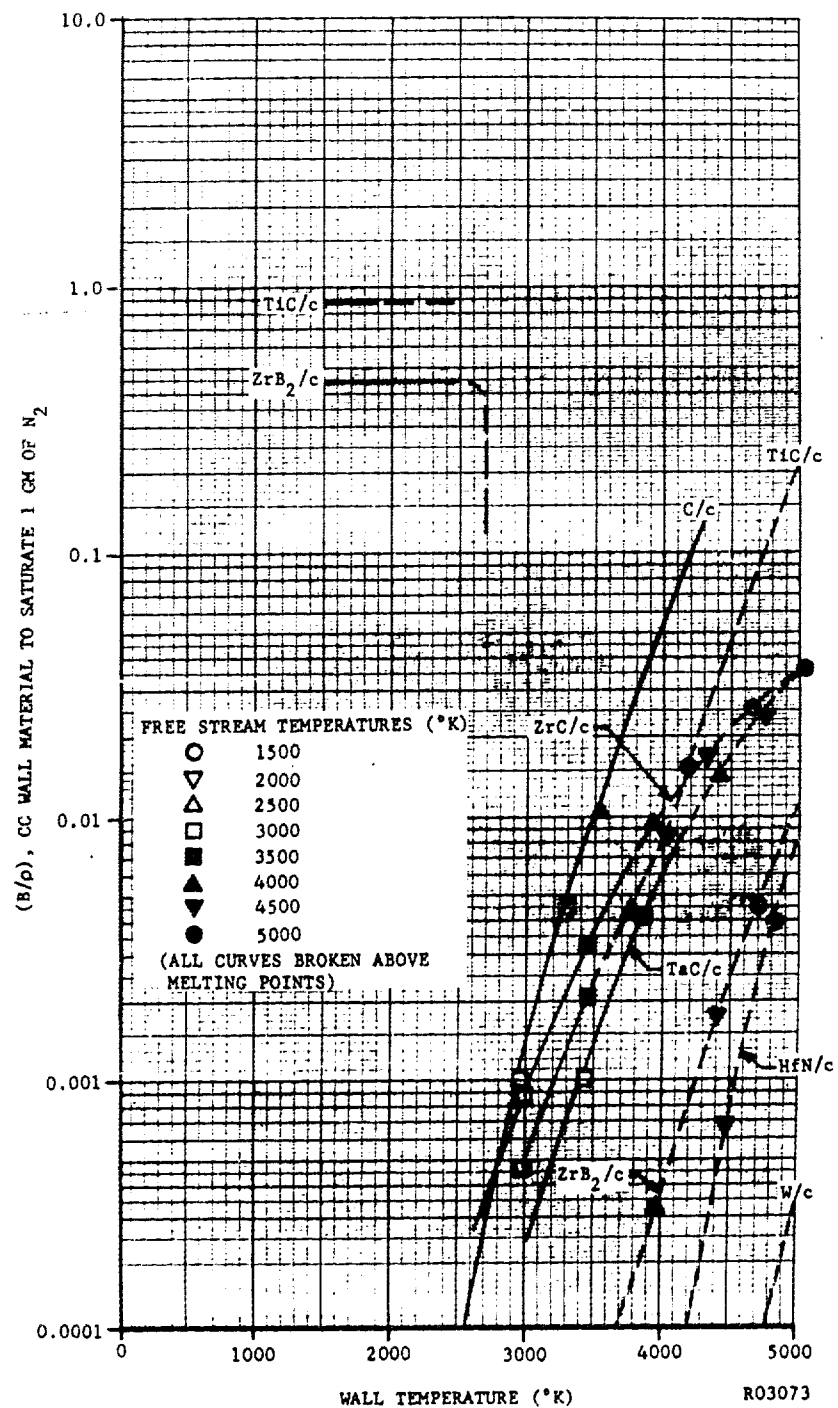


FIGURE 15. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO N_2 AT 1000 PSIA

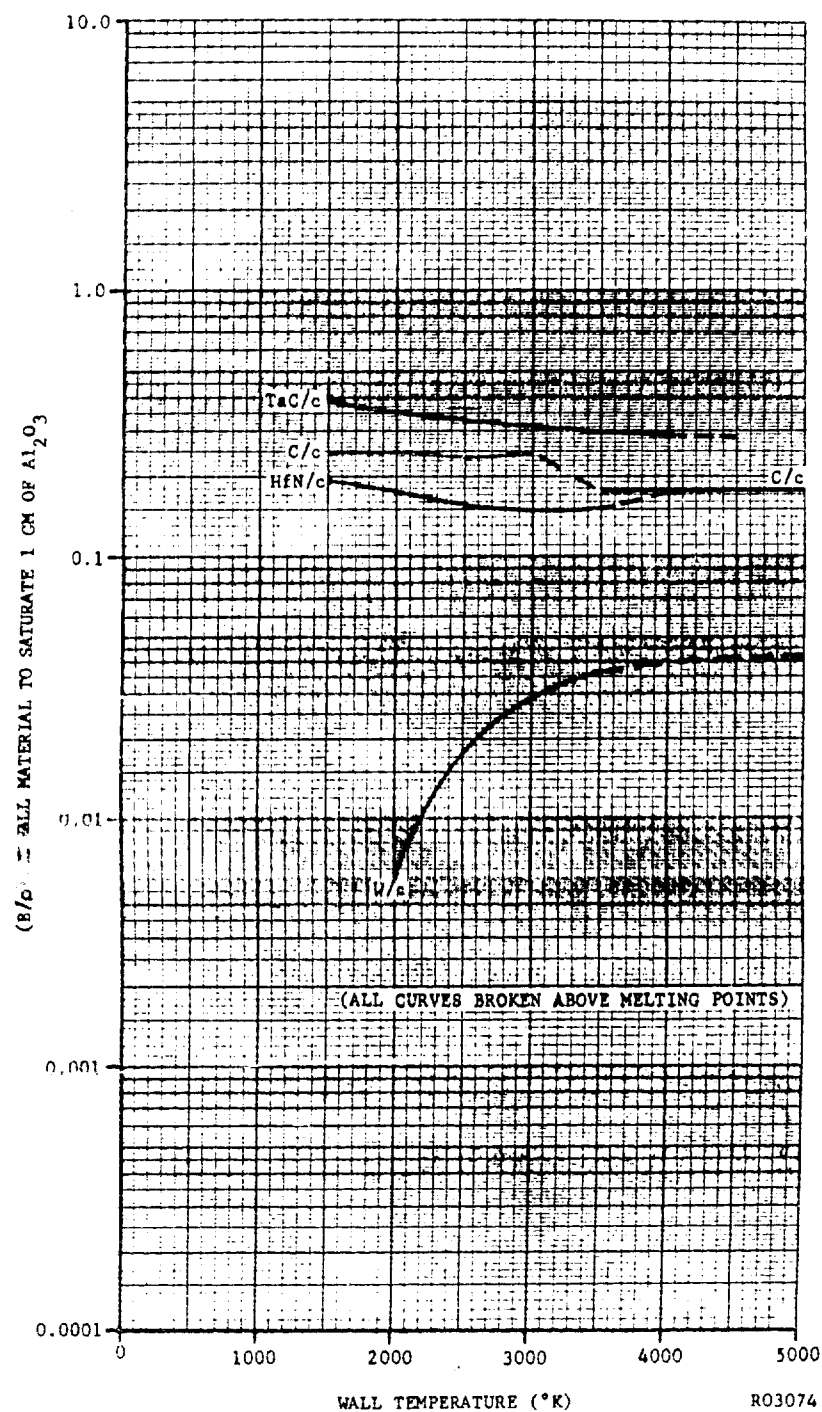


FIGURE 16. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO Al_2O_3/c AT THE MIXED VAPOR PRESSURES OVER THE TWO CONDENSED PHASES

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coefficients for the rocket nozzle environment, actual erosion rates themselves have not been predicted for the "pure" species.

In addition to the correlations of "isothermal" $\frac{B}{\rho}$ versus wall temperature, corrosion heat effects also have been considered, based upon the "adiabatic saturation" model assuming an enthalpy balance between free stream gas, virgin wall material, and saturated mixture at the wall. Accordingly, points corresponding to various hypothetical "free stream" temperatures are shown on the curves of $\frac{B}{\rho}$ versus wall temperature in Figures 3 through 16. The balance between free stream and saturated wall temperatures does depend on the assumption of unity Lewis and Prandtl numbers, and hence lacks some of the fundamental significance of the simple isothermal case.

In view of the small variations of densities with temperature, all values of $\frac{B}{\rho}$ were based upon room-temperature densities for the refractories in question. The curves of $\frac{B}{\rho}$ versus wall temperature in Figures 3 through 16 also have been drawn as broken above the respective melting points, inasmuch as the treatment assuming only chemical attack loses meaning where liquid run-off occurs. (In rating materials, no refractory shall be considered resistant to erosion at temperatures above its melting point.) Densities and melting points for the nine refractory materials considered are taken to be the following:

Refractory	Density (ρ_{298})	Melting Point, °K
C/c	~ 1.90	----
W/c	19.3	3650
TaC/c	14.5	4100
HfN/c	14.0	3580
TiC/c	4.9	3410
ZrC/c	6.7	3770
ZrB ₂ /c	6.09	3320
MgO/c	3.7	3070
HfO ₂ /c	9.68	3170

Relative ratings of refractory materials are discussed separately for the fourteen "pure" species considered.

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AlF₃ - Figure 3

Of the four refractories studied, graphite (C/c) generally appears the most resistant to chemical attack by AlF₃, although TaC/c does give slightly lower $\frac{B}{Q}$ values at wall temperatures from $\sim 3800^{\circ}\text{K}$ up to its melting point of 4100°K . Tungsten (W/c) also is reasonably resistant up to its respective melting point. The only material showing serious theoretical attack is HfN/c, which is oxidized nearly quantitatively by the AlF₃ \rightarrow AlF reaction at all temperatures. Comparisons on the basis of "free stream" temperatures show almost the same relative ratings except that W/c should be cooled to below its melting point of 3650°K even at bulk flow temperatures well above 4000°K .

BF₂ - Figure 4

All four refractories considered are indicated to react nearly quantitatively with BF₂ to form borides at wall temperatures below about 2000°K ; only graphite, yielding B₄C/c, exhibits reasonably low $\frac{B}{Q}$ values. It is questionable, however, whether metal boride formation is kinetically likely at these conditions. Thus, at least in the cases of TaC/c and W/c, the higher $\frac{B}{Q}$ values at low temperatures might be partially discounted.

At high wall temperatures, C/c and TaC/c both show excellent resistance to corrosion up to about 4000°K . Tungsten also is reasonably resistant up to its melting point of 3650°K , and should furthermore be able to withstand "free stream" temperatures of over 4000°K without melting.

Hafnium nitride (HfN/c) reacts quantitatively with BF₂ to form HfB₂/c and Hf-F species over the entire temperature range, and thus cannot be considered satisfactory for use in this atmosphere.

BF₃ - Figure 5

Graphite (C/c) generally is the most resistant to corrosion of the four refractories considered with BF₃, although all materials begin to

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show some significant attack at wall temperatures above 3000-3500°K. In the case of tungsten, in fact, the reaction to form WF_6 and BF occurs nearly quantitatively at its melting point of 3650°K. Cooling effects, however, are significant with TaC/c and W/c, so that these two materials show reasonably good corrosion resistance at "free stream" temperatures up to nearly 4000°K.

Contrary to the case for BF_2 , metal boride formation with BF_3 occurs only with HfN/c, which quantitatively yields HfB_2 /c, Hf-F species, and correspondingly high $\frac{B}{C}$ values over the entire range of temperature.

BOF - Figure 6

Tungsten (W/c) is the only one of the four refractories studied showing good corrosion resistance to BOF. Above the tungsten melting point of 3650°K, therefore, no material can be rated as satisfactory in this environment.

Graphite (C/c) and tantalum carbide (TaC/c) both react stoichiometrically with BOF to form BF and CO at wall temperatures above about 2500°K and above about 3500°K, respectively. Reaction cooling effects are large, but generally are still not sufficient to reduce corrosion to acceptable values at "free stream" temperatures greater than 2500°K. Hafnium nitride (HfN/c) reacts quantitatively with BOF over the entire temperature range, yielding HfO_2 /c, HfB_2 /c and Hf-F species.

BeF₂ - Figure 7

Of the four refractories considered with BeF_2 , C/c, W/c and TaC/c all show generally good corrosion resistance at wall temperatures up to their melting points, or, in the case of graphite, up to ~4000°K. The corrosion reactions are mildly endothermic in all three cases, but are not sufficiently so to provide cooling protection at "free stream" temperatures much above 4000°K. Except for the case of graphite volatilization at high temperatures, oxidation by virtue of the $BeF_2 \rightarrow BeF$ reaction generally is responsible for what attack does occur.

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Hafnium nitride (HfN/c) is the only material studied which exhibits appreciable theoretical corrosion by BeF_2 over the entire temperature range. The $\frac{B}{P}$ values in the vicinity of 2500°K wall temperature are moderately low, however, and owing to the significant cooling effect, do apply for "free stream" temperatures up to $\sim 3500^\circ\text{K}$. Nevertheless, HfN/c must be rated significantly poorer than either C/c, W/c or TaC/c.

CO - Figure 8

Of the seven refractory materials considered with CO, only HfN/c shows severe corrosion over the entire temperature range. The corrosion products for HfN/c and CO are HfO_2/c plus C/c below 2550°K , and HfO_2/c plus HfC/c above this temperature. The refractories TiC/c and ZrC/c are oxidized stoichiometrically by CO, but only at wall temperatures of 2000°K and below. At 2500°K , the oxidation becomes nil. Tungsten also shows corrosion by virtue of the formation of WC/c at low wall temperatures, but this reaction may be kinetically unlikely at these conditions.

Other than the preceding, all materials considered, including TaC/c, ZrB_2/c , and C/c, show excellent resistance to attack by CO at temperatures up to their melting points, or, in the case of C/c, until simple volatilization becomes important.

CO₂ - Figure 9

Of the nine refractory materials considered with CO₂, only the oxides MgO/c and HfO_2/c show some satisfactory resistance to chemical corrosion. Use of these two refractories, however, must take into account their questionable physical properties and their low melting points (3070°K and 3170°K , respectively).

The remaining seven refractories are all attacked nearly stoichiometrically by CO₂, forming CO in the case of C/c, gaseous W_3O_9 in the case of W/c, and condensed metal oxides with the others. Over the range of

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wall temperatures considered, tungsten yields slightly lower $\frac{B}{Q}$ values than the other materials, although if "free stream" temperature is taken as the variable, graphite is more resistant below 2500°K, owing to a pronounced cooling effect.

HCl - Figure 10

Tungsten and graphite both exhibit excellent resistance to corrosion by HCl at wall temperatures up to 3650°K, the melting point of tungsten. Tantalum carbide (TaC/c) becomes increasingly resistant to attack at the higher wall temperatures, and, between 3650°K and its own melting point of 4100°K, appears to be the best choice. On the basis of "free stream" temperature, however, TaC/c loses its melting point advantage over W/c, owing to an exothermic heat of reaction.

The remaining four refractories considered with HCl (HfN/c, TiC/c, ZrC/c and ZrB₂/c) all show moderate to severe theoretical corrosion over the entire temperature range, resulting from near-stoichiometric reactions forming gaseous metal chlorides and hydrogen.

HF - Figure 11

Only graphite, of the seven refractories considered, exhibits good resistance to corrosion by HF, and only at wall temperatures below 3500°K ("free stream" temperatures below 4000°K). Tungsten and tantalum carbide are attacked nearly stoichiometrically by HF at low temperatures, but are somewhat more resistant at higher temperatures, so that they may be rated roughly equivalent to graphite at temperatures in the vicinities of their melting points.

The four remaining refractories HfN/c, TiC/c, ZrC/c and ZrB₂/c undergo nearly quantitative reactions with HF throughout most of the temperature range, yielding metal fluorides and hydrogen.

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H₂ - Figure 12

The only refractory material of the seven considered that is severely attacked by H₂ under equilibrium conditions is graphite (C/c). At temperatures below 2000°K the primary reaction product is CH₄; above 2500°K, the products are C₂H₂ and C₂H. The hydrogenolysis of graphite is recognized to be somewhat kinetically limited in practice.

The other six materials studied, W/c, TaC/c, HfN/c, TiC/c, ZrC/c and ZrB₂/c, all show excellent resistance to corrosion by H₂ at temperatures up to their respective melting points. Condensed metal hydrides, however, particularly HfH₂/c, ZrH₂/c and TiH₂/c, were not considered in the calculations from which the curves in Figure 12 were derived.

H₂O - Figure 13

All seven refractories considered show severe theoretical corrosion by H₂O. The most nearly resistant material over the entire temperature range is tungsten (W/c), which is also the only refractory not oxidized quantitatively at these conditions. Nevertheless, $\frac{B}{P}$ values for tungsten are high. The remaining six materials are converted to CO, in the case of C/c, and condensed metal oxides in the cases of TaC/c, HfN/c, TiC/c, ZrC/c and ZrB₂/c.

LiF - Figure 14

At temperatures much below 3000°K, systems consisting only of a refractory material and pure LiF are completely condensed at 1000 psia. Restricting attention to the higher temperature regime, TaC/c and W/c show excellent resistance to corrosion by LiF up to their respective melting points (4100°K and 3650°K). Graphite also is quite resistant up to the temperature (4000-4500°K) at which vaporization becomes important. Of the four materials considered, only HfN/c exhibits appreciable theoretical

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corrosion at elevated wall temperatures. Even then, owing to the pronounced cooling effect, HfN/c may be moderately resistant to attack if "free stream" temperature is taken as the basis.

N₂ - Figure 15

Of the seven refractories considered with a N₂ environment, TiC/c, ZrB₂/c and possibly TaC/c and ZrC/c exhibit severe theoretical corrosion at temperatures in the range 1500-2500°K, owing to the stoichiometric formation of metal nitrides. As in the cases of boride and carbide formation at low temperatures, the formation of nitrides at such conditions may, however, be kinetically unlikely.

At higher wall temperatures, nearly all the materials considered were quite resistant to corrosion by N₂ up to their melting points; the very lowest $\frac{B}{Q}$ values were found for W/c and for HfN/c. Only in the case of graphite did theoretical attack begin to become appreciable above 3500°K, owing to the formation of gaseous CN.

Al₂O₃/c - Figure 16

Inasmuch as most systems of a refractory material plus Al₂O₃/c would be completely condensed at 1000 psia except at very high temperatures, a comparison of equilibrium corrosion behavior for a fixed total pressure was not considered meaningful. Instead, calculations for Al₂O₃/c and the four refractories C/c, W/c, TaC/c, and HfN/c were carried out for variable total pressures, such that the two condensed phases, Al₂O₃/c and the refractory, would both be present at equilibrium. From phase-rule considerations, only one such mixed "vapor pressure" and one gas composition could exist for any given temperature.

Comparison of $\frac{B}{Q}$ curves in Figure 16 indicates that W/c is the most resistant to attack by Al₂O₃/c at these conditions, yielding only moderate theoretical corrosion up to its melting point of 3650°K. In contrast, C/c, TaC/c and HfN/c all attacked almost quantitatively by

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$\text{Al}_2\text{O}_3/\text{c}$, yielding CO in the case of graphite and Ta/c and HfO_2/c in the case of the metallic refractories. Vapor pressures over the two phases also were lowest for W/c plus $\text{Al}_2\text{O}_3/\text{c}$; a total pressure of 1000 psia would not be reached except at a temperature above 5000°K , i.e., much higher than the melting point of tungsten. Total pressures of 1000 psia would be reached instead at about 2900°K for C/c, 3800°K for TaC/c, and 3500°K for HfN/c. At temperatures higher than the preceding, "boiling" would take place if the two condensed phases were in contact at 1000 psia total pressure.

Conclusion

Relative theoretical ratings for refractory materials exposed to the fourteen propellant species studied are summarized in Table III. It is seen that with only a few exceptions, the best policy from the standpoint of corrosion apparently fits the empirical rule of choosing tungsten for wall temperatures up to its melting point (3650°K), and then choosing graphite for higher wall temperatures.

TABLE III
RELATIVE THEORETICAL RATINGS OF REFRACTORY MATERIALS
EXPOSED TO 14 DIFFERENT PROPELLANT SPECIES

	<u>C/c</u>	<u>W/c</u>	<u>TaC/c</u>	<u>HfN/c</u>	<u>TiC/c</u>	<u>ZrC/c</u>	<u>ZrB₂/c</u>	<u>MgO/c</u>	<u>HfO₂/c</u>
AlF ₃	(X)	X	X	0	-	-	-	-	-
BF ₂	(X)	?	?	0	-	-	-	-	-
BF ₃	(X)	X	X	0	-	-	-	-	-
BOF	0	(X)	0	0	-	-	-	-	-
BeF ₂	X	X	(X)	0	-	-	-	-	-
CO	X	?	(X)	0	0	0	X	-	-
CO ₂	0	(0)	0	0	0	0	0	X	(X)
HCl	X	(X)	X	0	0	0	0	-	-
HF	(X)	0	0	0	0	0	0	-	-
H ₂	0	(X)	X	X	X	X	X	-	-
H ₂ O	0	(0)	0	0	0	0	0	-	-
LiF	X	X	(X)	0	-	-	-	-	-
N ₂	X	(X)	?	X	?	?	?	-	-
Al ₂ O ₃ /c	0	(X)	0	0	-	-	-	-	-

KEY: X "acceptable"
 ? questionable
 0 not "acceptable"
 - not studied

(Best choices are circled for each species.)

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3.2 THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO REAL PROPELLANT SYSTEMS

In addition to the studies of theoretical corrosion of refractory materials by "pure" combustion species, a few similar calculations were made for materials exposed to real propellant mixtures. The comparisons to be discussed in the following paragraphs include such systems as F_2/H_2 , aluminumized "hot solid", and "NF"- "BOF" type combinations.

F_2/H_2 - Figure 17

Theoretical saturation parameters ($\frac{B}{Q}$) for four refractories (TiC/c, TiN/c, ZrC/c and ZrO_2/c) exposed to a F_2/H_2 system at 500 psia are compared in Figure 17. The principal species present in the "free stream" combustion mixture at the throat are HF, H_2 and H. All the materials considered showed appreciable theoretical corrosion through the temperature region of interest. Considering that ZrO_2/c would also undergo melting ablation at wall temperatures above $2950^\circ K$, perhaps the most resistant of the four would be TiC/c. However, graphite and (possibly) tungsten, neither of which were considered with this particular mixture, would both probably be rated more satisfactory than TiC/c.

"Hot Solid" - Figures 18 and 19

Theoretical saturation values are plotted in Figure 18 for C/c, W/c and TaC/c refractories exposed to the combustion products of an aluminumized solid propellant containing a perchlorate oxidizer. The calculations are for a throat pressure of 405.8 psia, corresponding to a chamber pressure of 700 psia. The major species present in the "free stream" at the throat are CO, H_2O , H_2 , H, N_2 , HCl and Al_2O_3/c . Under these conditions, tungsten (W/c) is clearly the most resistant to attack at wall temperatures up to its melting point of $3650^\circ K$. Since tungsten, however, would undergo melting ablation at the wall temperature corresponding to the $3826^\circ K$ throat stagnation temperature, none of the three materials can be rated completely satisfactory for this service.

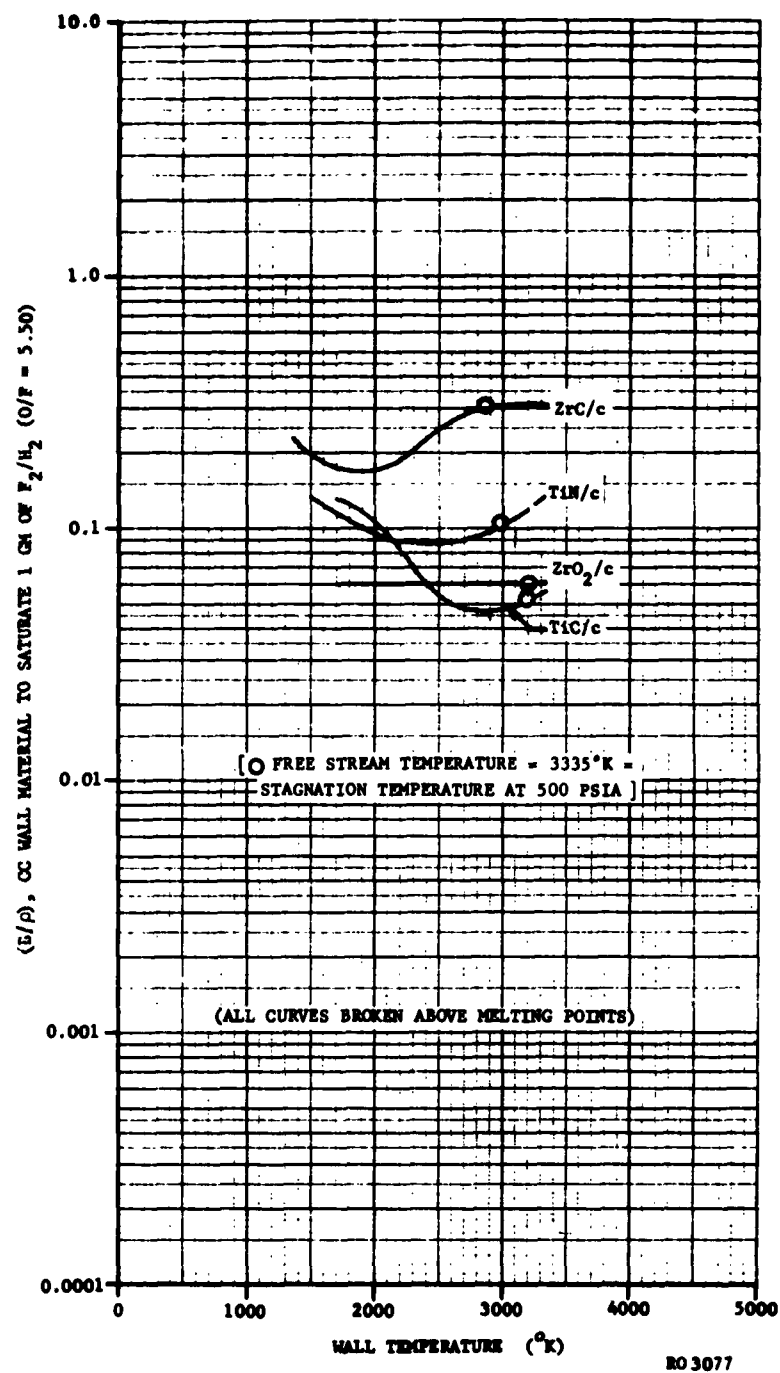


FIGURE 17. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO F_2/H_2 ($O/F = 5.50$) AT 500 PSIA

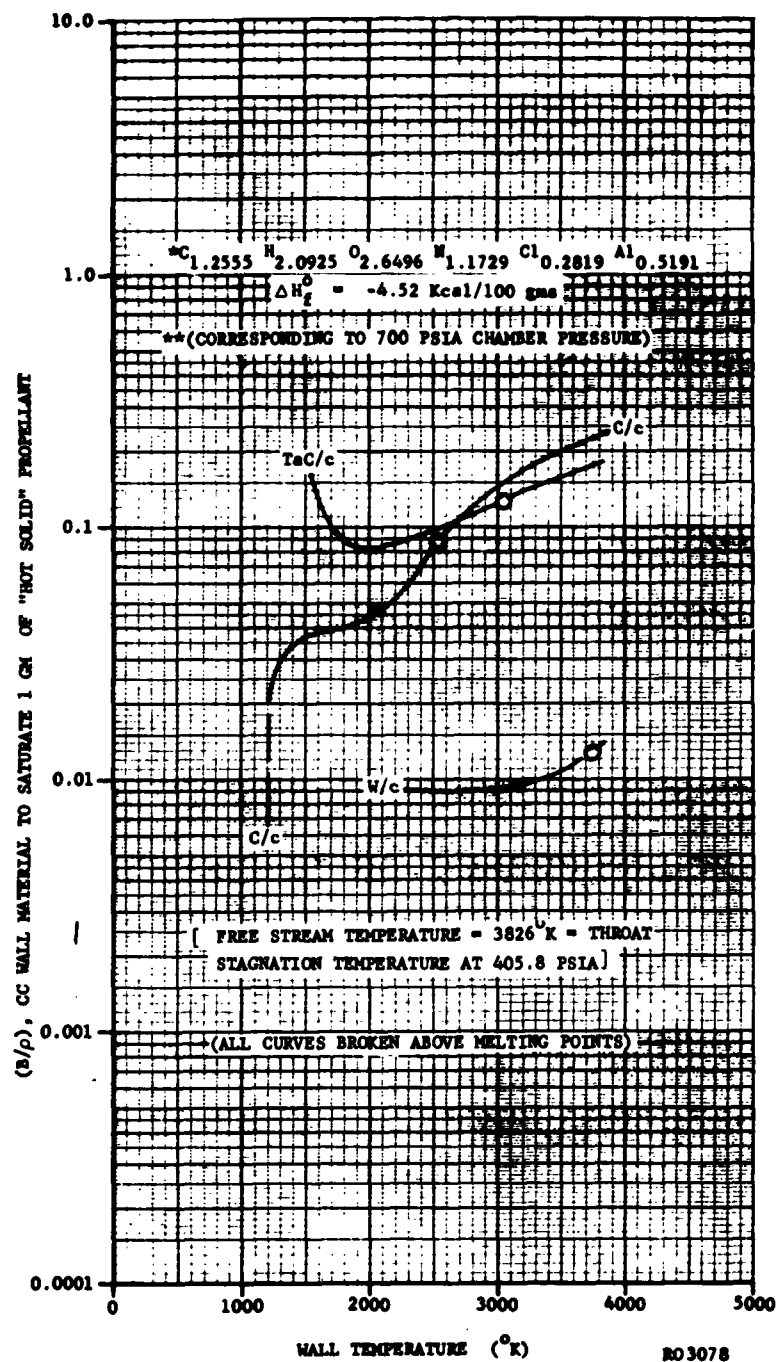


FIGURE 18. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO "HOT SOLID" PROPELLANT* AT 405.8 PSIA THROAT PRESSURE**

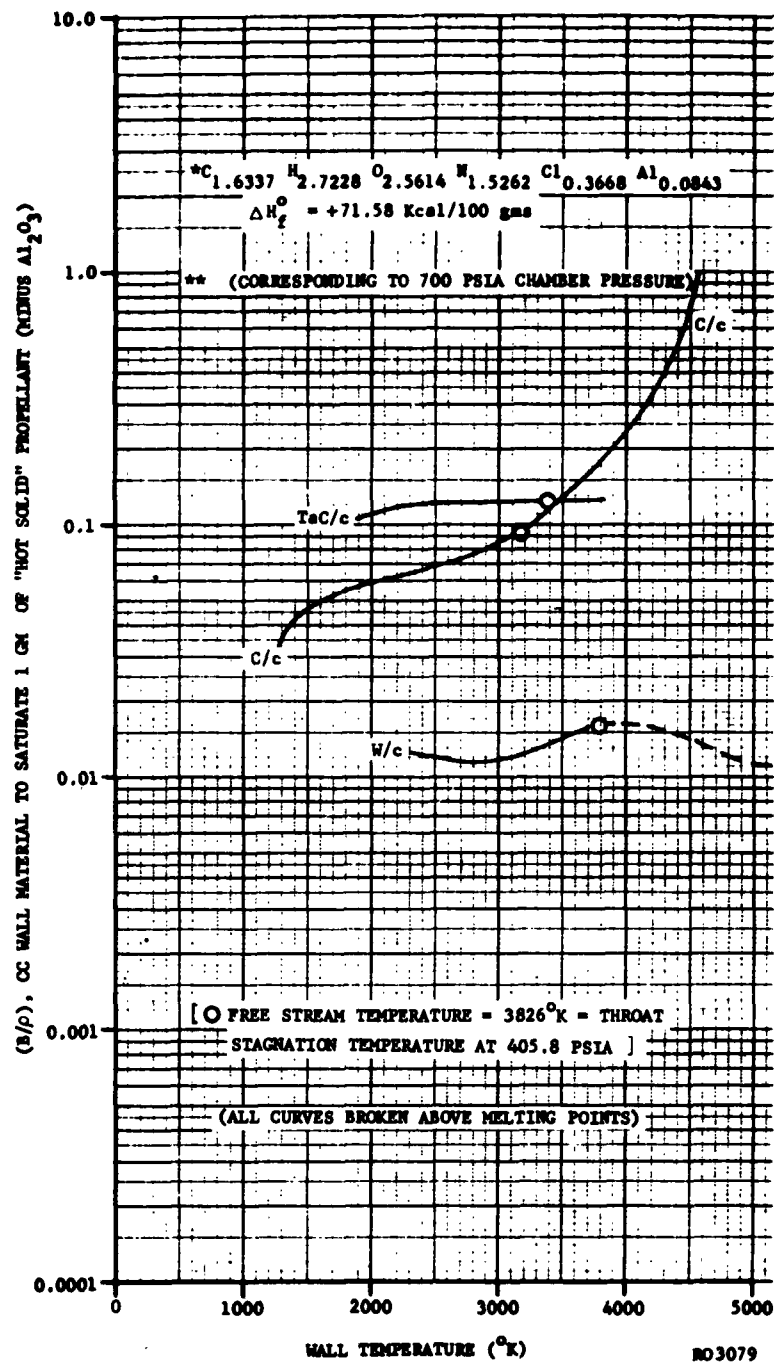


FIGURE 19. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO "HOT SOLID" PROPELLANT (MINUS Al_2O_3) * AT 405.8 PSIA THROAT PRESSURE **

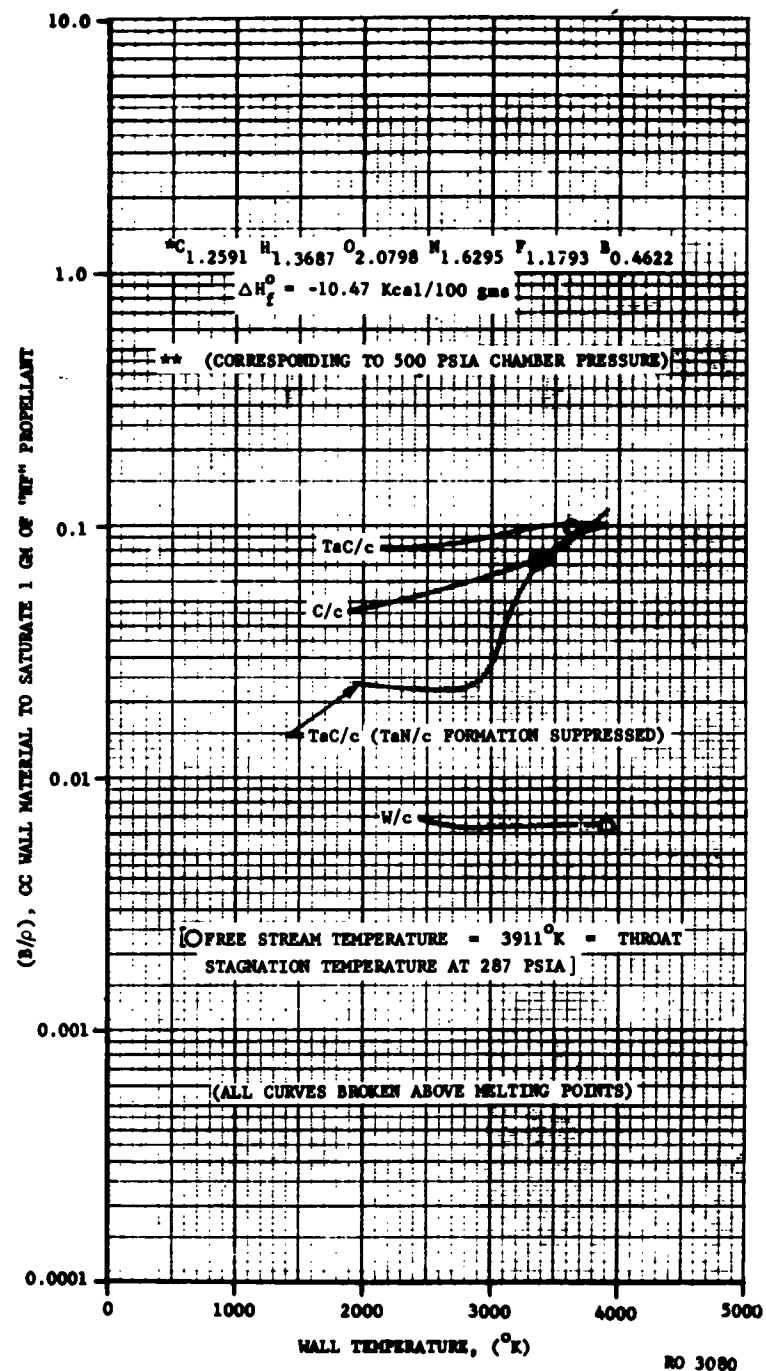
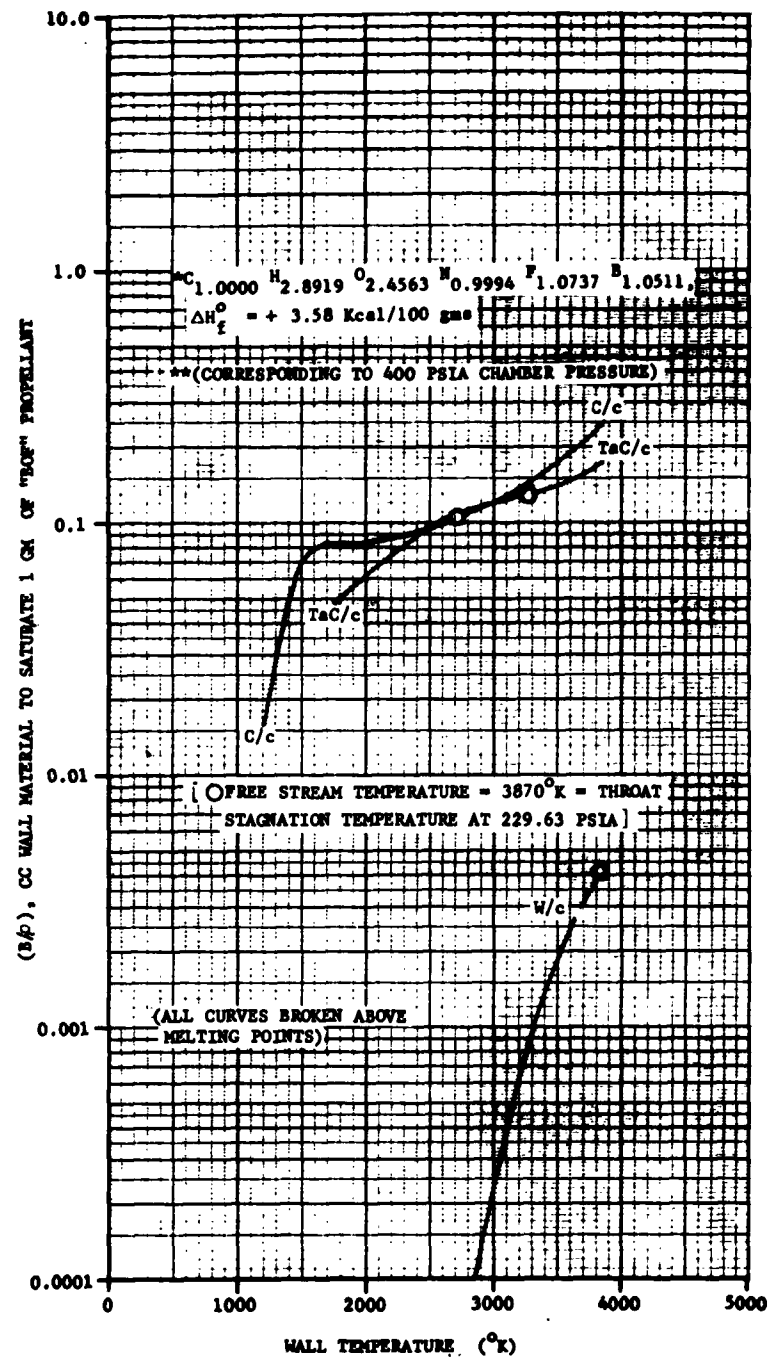


FIGURE 20. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO "NF" PROPELLANT* AT 287 PSIA THROAT PRESSURE**



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FIGURE 21. THEORETICAL RATING OF REFRACTORY MATERIALS EXPOSED TO SIMULATED "BOF" PROPELLANT* AT 229.63 PSIA THROAT PRESSURE**

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In the case of a solid propellant yielding condensed Al_2O_3 particles, theoretical corrosion calculations can be made either for the assumption that the particles react with the wall in the same proportion as their bulk gas concentration, as in the preceding example, or for the alternative assumption that the particles remain in the turbulent core and never penetrate the boundary layer. In this second case, which is shown in Figure 19 for the three refractories C/c, W/c and TaC/c, the Al_2O_3 /c present in the mixture at throat stagnation conditions has been "removed" from the system prior to equilibration with the wall material. It is seen that this assumption yields only minor changes in absolute $\frac{B}{\phi}$ values versus wall temperatures, and no changes at all in the relative ratings. In other words, the corrosivity of the gaseous phase is of comparable magnitude to that of the Al_2O_3 /c.

Calculations of theoretical corrosion for an approximate simulation of the "hot solid" propellant at a slightly different pressure (not shown) indicated only small differences from the results given in Figure 18 and 19.

"NF"-"BOF" Types - Figures 20 and 21

Equilibrium corrosion parameters for C/c, W/c and TaC/c refractories exposed to an "NF" solid propellant at 287 psia throat pressure (500 psia chamber pressure) are shown in Figure 20. The major combustion products of this composition at the throat conditions are CO_2 , CO, H_2O , H_2 , H, N_2 , HF and BOF. Tungsten once again is seen to be the most resistant to attack, but owing to melting ablation, still is not capable of withstanding the 3911°K throat stagnation temperature. The relative ranking of TaC/c and C/c varies, depending on whether TaN/c formation is assumed to be kinetically likely with the former, but in any case, attack should be appreciable with either of these two materials.

In Figure 21 the three materials C/c, W/c and TaC/c again are compared, this time for exposure to an approximate simulation of a "BOF"

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propellant at 229.63 psia throat pressure (400 psia chamber pressure). The major species here are CO, H₂O, H₂, H, N₂, HF and BOP. Inasmuch as the chemical composition is not too different from that of the "NF" propellant, the relative ratings are much the same, with W/c showing excellent corrosion resistance at wall temperatures up to its melting point, while C/c and TaC/c are attacked substantially throughout the temperature regime. (The case of TaN/c formation suppressed was not considered for TaC/c in this comparison.)

SECTION 4

PREDICTION OF ACTUAL EROSION RATES

In the Fifth Quarterly Report⁵ under this contract, a preliminary study was presented which attempted to assess the validity of the "simplified Denison" ablation model² assuming equilibrium at the wall with Lewis and Prandtl numbers taken to be unity. A three-way comparison was made between predicted erosion rates, rates calculated by Jones and Delaney⁸ from kinetic theory, and rates determined experimentally by NASA-Lewis.⁹ The systems considered were graphitic nozzle inserts exposed to two state-of-the-art solid propellants and to two advanced solid formulations, with nominal chamber pressures of 1000 psia for the former and 500 psia for the latter.

The erosion rates predicted in this study were estimated from equation (2) or equation (3) for the unsteady-state simplified Denison model with wall temperature assumed to be known as a function of time. Owing to the relatively short duration of the firings being considered, the steady-state adiabatic saturation model (equation (1)) was not applicable. The enthalpy heat transfer coefficient ($\frac{h_c}{C_p}$) was estimated using the Bartz¹³ equation for rocket nozzle heat transfer, even though this correlation was recognized to be only an approximation. For those propellants yielding condensed Al_2O_3/c as a combustion product, theoretical corrosion calculations were performed both for the assumption that the Al_2O_3/c particles diffuse to the wall in proportion to their concentration,

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and for the alternative assumption that no $\text{Al}_2\text{O}_3/\text{c}$ ever reaches the wall. (Strictly speaking, the Denison approach¹⁰ is limited to all-gas systems, and thus should be applicable only to the latter case.)

The experimental data considered were determined at NASA-Lewis⁹ for three types of graphite nozzles (ATJ, Speer 3499, and ZT) exposed to the combustion products of Arcite 368 and Arcite 373, two state-of-the-art solid propellants. The former of these is a 4700°F nonmetallized composition containing the elements CHONCl , and the latter, a 5500°F aluminized formulation including the elements CHONClAl . Inasmuch as the unpublished results²¹ for test firings with Arcite 373 showed erosion completely obscured by deposition of a layer of $\text{Al}_2\text{O}_3/\text{c}$, only the data for Arcite 368 were considered for comparison.

Predictions of theoretical corrosion, using the simplified Denison model assuming equilibrium reaction, averaged almost a full order of magnitude higher (~ 35 mils/second) than the maximum rates calculated (~ 5 mils/second) for the NASA tests with Arcite 368 and graphite nozzles. The discrepancy was explained by examination of surface temperatures, which, as estimated by a somewhat doubtful extrapolation of thermocouple readings for the ATJ firing, never exceeded 1800°K during the 30-second duration of the test. At temperatures this low, surface reaction rates might well be nil, rather than infinitely rapid as was assumed in the equilibrium model. From chamber pressure traces taken during the NASA tests, it appears that most of the measured erosion of graphitic nozzles was purely mechanical in nature, and occurred during the first five seconds of firing.

Predictions based upon the simplified Denison approach also were compared to erosion rates calculated by Jones and Delaney⁸ for graphite nozzles exposed to various propellant systems. In most cases, the calculations of Jones and Delaney were based upon finite reaction rates, rather than attainment of complete chemical equilibrium. Independent correlations for overall heat transfer and for overall mass transfer moreover were employed, so that the assumption of unity Lewis numbers was

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not required. For these reasons, the predictions of Jones and Delaney would be expected to differ from those based upon the simple model, and should probably be better.

In the case of the Arcite 368 propellant, and for comparable conditions of temperature, pressure, and geometry, the "simplified Denison" predictions assuming equilibrium corrosion averaged an order of magnitude higher than the erosion rates calculated by Jones and Delaney for kinetically-limited reaction. The two methods, however, were in rough agreement (factor of only 1.5-1.7) for the special case in which Jones and Delaney also assumed complete equilibrium at the wall. Neither method predicted, or could predict, the mechanical erosion effect previously described as having occurred in the NASA experiments with this system.

No comparison with meaningful test data was possible for Arcite 373 propellant, nor for the two advanced formulations, "NP"* and "NF"** , respectively. Comparisons were made between "simplified Denison" predictions and the more rigorous calculations of Jones and Delaney for these systems, however, and showed graphite erosion rates estimated by the simple equilibrium model high by a factor of at least 3 for Arcite 368 and for "NP", and high by a factor of about 8 for the "NF" case. Inasmuch as kinetic limitations probably become unimportant at the high ($\sim 3000^{\circ}\text{K}$) wall temperatures involved, the discrepancies between the two methods must arise either from (1) failure of the Denison approach to allow for Lewis number effects, or from (2) omission of important species or reactions in the calculations by Jones and Delaney. (The BOF-graphite reaction, for example, was neglected in the "NF" propellant case.)

In conclusion, the simplified Denison-model approach assuming chemical equilibrium at the refractory wall is not valid for predicting

* "NP" = 6600°F solid propellant, elements CHONCLiAl

**"NF" = 6700°F solid propellant, elements CHONFB

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transient erosion rates with most state-of-the-art solid propellant systems, owing to the low temperatures involved. For advanced solid propellants yielding higher flame temperatures, the simple method does show some promise, at least for making qualitative comparisons for different refractories. Greater quantitative validity for high-temperature systems might be achieved if the simplified Denison model could be modified, particularly to account for the effects of non-unity Lewis numbers.

SECTION 5

PROPELLANT PERFORMANCE STUDIES

Theoretical performance calculations for certain unclassified and classified binary liquid propellant combinations were carried out as part of this contract. The "pressure profile" option of the Aeronutronic Rocket Propellant Performance Program was utilized in determining expansion performance parameters at integer area ratios from 1 to 50, and, in turn, ideal performance values at given epsilons for ambient pressures ranging from sea level down to vacuum. Thus, propellant systems could be compared for specific applications, rather than on some arbitrary basis such as optimum expansion to one atmosphere.

Calculations were run for two chamber pressures: 1000 psia and 300 psia. In general, five mixture ratios at each pressure were considered for each propellant combination studied. The latest JANAF¹⁴ thermodynamic data available at the time were used, with a large number of possible combustion species included. Both the frozen and the equilibrium expansion cases were considered.

The results for eleven unclassified systems ($\text{ClF}_3/\text{N}_2\text{H}_4$, F_2/H_2 , $\text{H}_2\text{O}_2/\text{B}_5\text{H}_9$, $\text{N}_2\text{F}_4/\text{B}_5\text{H}_9$, $\text{N}_2\text{H}_4/\text{B}_5\text{H}_9$, $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, $\text{OF}_2/\text{B}_2\text{H}_6$, $\text{OF}_2/\text{B}_5\text{H}_9$, $\text{OF}_2/\text{N}_2\text{H}_4$, O_2/H_2 , and $\text{O}_2/\text{RP-1}$) have been reported in Volume II of the Second Quarterly Report⁶. Similarly, the data for ten classified systems have been presented in Volume III⁷ of that report. Inasmuch as the method, computer program, and results were discussed fully at that time, the reader is referred to these two volumes for further information.

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APPENDIX A

THERMODYNAMIC DATA FOR C_2H , THREE W
SPECIES, AND FIVE Zr SPECIES

TERMOODYNAMIC FUNCTIONS OF $C_2H_2(g)$

$$\Delta H_f^\circ = 112.1 \text{ kcal/mol}$$

T (°K)	$F-H_{298}$ (cal/mol-°K)	S (cal/mol-°K)	Cp (cal/mol-°K)	H_{298} (kcal/mol)
298.15	49.592	49.592	8.872	0
300.00	49.592	49.646	8.889	.016
400.00	49.950	52.315	9.657	.946
500.00	50.651	54.535	10.235	1.942
600.00	51.461	56.444	10.717	2.950
700.00	52.296	58.129	11.141	4.083
800.00	53.121	59.642	11.523	5.217
900.00	53.923	61.019	11.866	6.386
1000.00	54.697	62.286	12.174	7.589
1100.00	55.441	63.459	12.449	8.820
1200.00	56.155	64.553	12.692	10.077
1300.00	56.841	65.577	12.907	11.358
1400.00	57.500	66.541	13.097	12.658
1500.00	58.133	67.450	13.265	13.976
1600.00	58.742	68.311	13.413	15.310
1700.00	59.330	69.129	13.544	16.658
1800.00	59.896	69.906	13.660	18.019
1900.00	60.442	70.647	13.763	19.390
2000.00	60.970	71.356	13.854	20.771
2100.00	61.481	72.034	13.936	22.160
2200.00	61.976	72.684	14.009	23.558
2300.00	62.455	73.308	14.074	24.962
2400.00	62.920	73.908	14.133	26.372
2500.00	63.371	74.486	14.186	27.788
2600.00	63.809	75.043	14.234	29.209
2700.00	64.235	75.581	14.278	30.635
2800.00	64.650	76.101	14.318	32.065
2900.00	65.053	76.605	14.354	33.498
3000.00	65.447	77.092	14.387	34.935
3100.00	65.830	77.564	14.417	36.376
3200.00	66.204	78.022	14.444	37.819
3300.00	66.569	78.467	14.470	39.264
3400.00	66.925	78.899	14.493	40.713
3500.00	67.273	79.320	14.515	42.163
3600.00	67.613	79.729	14.535	43.616
3700.00	67.946	80.127	14.553	45.070
3800.00	68.272	80.516	14.571	46.526
3900.00	68.591	80.894	14.587	47.984
4000.00	68.903	81.264	14.602	49.443
4100.00	69.209	81.625	14.615	50.904
4200.00	69.509	81.977	14.628	52.367
4300.00	69.803	82.321	14.640	53.830
4400.00	70.091	82.658	14.652	55.295
4500.00	70.374	82.987	14.662	56.760
4600.00	70.652	83.310	14.672	58.227
4700.00	70.924	83.625	14.682	59.695
4800.00	71.192	83.935	14.691	61.163
4900.00	71.455	84.238	14.699	62.633
5000.00	71.714	84.535	14.707	64.103
5100.00	71.968	84.826	14.714	65.574
5200.00	72.218	85.112	14.721	67.046
5300.00	72.464	85.392	14.728	68.518
5400.00	72.706	85.668	14.734	69.992
5500.00	72.944	85.938	14.740	71.465
5600.00	73.179	86.204	14.746	72.940
5700.00	73.410	86.465	14.751	74.414
5800.00	73.637	86.721	14.756	75.890
5900.00	73.861	86.974	14.761	77.366
6000.00	74.081	87.222	14.766	78.842

TERMODYNAMIC FUNCTIONS OF $\text{WCL}_3(\text{g})$

$$\Delta H_{298}^{\circ} = -119 \text{ KCAL/MOL.}$$

T (°K)	$-(H-H_{298})/T$ (cal/mole °K)	S (cal/mole °K)	C_p (cal/mole °K)	H_{298}^T (kcal/mole)
298.15	103.900	103.900	27.424	0
300.00	103.901	104.070	27.478	.051
400.00	105.006	112.273	29.373	2.907
500.00	107.147	118.933	30.251	5.893
600.00	109.588	124.495	30.728	8.944
700.00	112.065	129.254	31.015	12.032
800.00	114.479	133.409	31.202	15.144
900.00	116.791	137.092	31.330	18.271
1000.00	118.989	140.398	31.421	21.408
1100.00	121.074	143.396	31.489	24.554
1200.00	123.050	146.138	31.540	27.706
1300.00	124.924	148.664	31.580	30.862
1400.00	126.705	151.006	31.612	34.021
1500.00	128.398	153.188	31.638	37.184
1600.00	130.012	155.230	31.659	40.349
1700.00	131.553	157.150	31.676	43.516
1800.00	133.025	158.961	31.691	46.684
1900.00	134.436	160.675	31.703	49.854
2000.00	135.789	162.301	31.713	53.024
2100.00	137.089	163.849	31.723	56.196
2200.00	138.339	165.325	31.730	59.369
2300.00	139.543	166.735	31.737	62.542
2400.00	140.704	168.086	31.743	65.716
2500.00	141.826	169.382	31.749	68.891
2600.00	142.910	170.627	31.753	72.066
2700.00	143.959	171.826	31.758	75.242
2800.00	144.975	172.981	31.761	78.418
2900.00	145.960	174.095	31.765	81.594
3000.00	146.916	175.172	31.768	84.770
3100.00	147.844	176.214	31.770	87.947
3200.00	148.746	177.223	31.773	91.125
3300.00	149.624	178.200	31.775	94.302
3400.00	150.479	179.149	31.777	97.480
3500.00	151.311	180.070	31.779	100.657
3600.00	152.122	180.966	31.781	103.835
3700.00	152.914	181.836	31.783	107.014
3800.00	153.686	182.684	31.784	110.192
3900.00	154.440	183.510	31.785	113.370
4000.00	155.177	184.314	31.787	116.549
4100.00	155.897	185.099	31.788	119.728
4200.00	156.602	185.865	31.789	122.907
4300.00	157.291	186.613	31.790	126.085
4400.00	157.966	187.344	31.791	129.265
4500.00	158.627	188.059	31.792	132.444
4600.00	159.274	188.757	31.793	135.623
4700.00	159.909	189.441	31.793	138.802
4800.00	160.531	190.110	31.794	141.982
4900.00	161.141	190.766	31.795	145.161
5000.00	161.740	191.408	31.795	148.340
5100.00	162.328	192.038	31.796	151.520
5200.00	162.905	192.655	31.797	154.700
5300.00	163.473	193.261	31.797	157.879
5400.00	164.030	193.855	31.798	161.059
5500.00	164.577	194.439	31.798	164.239
5600.00	165.116	195.012	31.799	167.419
5700.00	165.645	195.575	31.799	170.599
5800.00	166.166	196.128	31.799	173.779
5900.00	166.678	196.671	31.800	176.958
6000.00	167.183	197.206	31.800	180.138

THEMODYNAMIC FUNCTIONS OF $\text{WCl}_6(\text{s})$

$$\Delta H_{f298}^\circ = -140 \text{ KCAL/MOLE}$$

T (°K)	$-(H-H_{298})/T$ (cal/mole °K)	S (cal/mole °K)	C_p (cal/mole °K)	H_{298}° (kcal/mole)
298.15	101.600	101.600	34.643	0
300.00	101.601	101.814	34.680	.064
400.00	102.980	112.000	36.005	3.604
500.00	105.623	120.108	36.618	7.242
600.00	108.612	126.816	36.951	10.922
700.00	111.631	132.528	37.152	14.628
800.00	114.560	137.499	37.282	18.350
900.00	117.358	141.895	37.372	22.083
1000.00	120.012	145.836	37.435	25.824
1100.00	122.525	149.406	37.483	29.570
1200.00	124.903	152.670	37.519	33.320
1300.00	127.156	155.674	37.547	37.073
1400.00	129.293	158.457	37.569	40.829
1500.00	131.325	161.050	37.587	44.587
1600.00	133.259	163.476	37.602	48.347
1700.00	135.105	165.756	37.614	52.107
1800.00	136.868	167.906	37.624	55.869
1900.00	138.555	169.941	37.633	59.632
2000.00	140.173	171.871	37.640	63.396
2100.00	141.727	173.708	37.646	67.160
2200.00	143.221	175.459	37.652	70.925
2300.00	144.659	177.133	37.656	74.690
2400.00	146.046	178.736	37.661	78.456
2500.00	147.384	180.273	37.664	82.222
2600.00	148.678	181.751	37.668	85.989
2700.00	149.929	183.172	37.671	89.756
2800.00	151.141	184.542	37.673	93.523
2900.00	152.316	185.864	37.676	97.291
3000.00	153.455	187.142	37.678	101.058
3100.00	154.562	188.377	37.680	104.826
3200.00	155.638	189.573	37.681	108.594
3300.00	156.684	190.733	37.683	112.362
3400.00	157.702	191.858	37.684	116.131
3500.00	158.693	192.950	37.686	119.899
3600.00	159.660	194.012	37.687	123.668
3700.00	160.602	195.044	37.688	127.437
3800.00	161.522	196.050	37.689	131.205
3900.00	162.420	197.029	37.690	134.974
4000.00	163.297	197.983	37.691	138.744
4100.00	164.154	198.914	37.692	142.513
4200.00	164.993	199.822	37.693	146.282
4300.00	165.813	200.709	37.693	150.051
4400.00	166.616	201.575	37.694	153.821
4500.00	167.402	202.422	37.695	157.590
4600.00	168.173	203.251	37.695	161.359
4700.00	168.928	204.062	37.696	165.129
4800.00	169.668	204.855	37.696	168.899
4900.00	170.394	205.632	37.697	172.668
5000.00	171.106	206.394	37.697	176.438
5100.00	171.806	207.141	37.698	180.208
5200.00	172.492	207.873	37.698	183.977
5300.00	173.167	208.591	37.698	187.747
5400.00	173.829	209.295	37.699	191.517
5500.00	174.480	209.987	37.699	195.287
5600.00	175.120	210.666	37.699	199.057
5700.00	175.750	211.334	37.700	202.827
5800.00	176.369	211.989	37.700	206.597
5900.00	176.978	212.634	37.700	210.367
6000.00	177.578	213.267	37.700	214.137

THERMODYNAMIC FUNCTIONS OF WF(g)

$$\Delta H_{f298}^{\circ} = 100 \text{ KCAL/MOLE}$$

T (°K)	$-(F-H_{298})/T$ (cal/mole °K)	S (cal/mole °K)	C _p (cal/mole °K)	H ₂₉₈ ^T (kcal/mole)
278.15	54.900	54.900	8.090	0
300.00	58.900	58.950	8.097	.015
400.00	59.222	61.325	8.400	.841
500.00	59.438	63.220	8.572	1.691
600.00	60.537	64.792	8.676	2.553
700.00	61.243	66.135	8.742	3.425
800.00	61.929	67.305	8.787	4.301
900.00	62.585	68.342	8.818	5.181
1000.00	63.208	69.273	8.841	6.064
1100.00	63.798	70.116	8.858	6.949
1200.00	64.357	70.887	8.871	7.836
1300.00	64.887	71.598	8.882	8.724
1400.00	65.390	72.256	8.890	9.612
1500.00	65.867	72.870	8.897	10.502
1600.00	66.325	73.444	8.902	11.391
1700.00	66.757	73.984	8.907	12.282
1800.00	67.175	74.493	8.910	13.173
1900.00	67.573	74.975	8.914	14.064
2000.00	67.955	75.432	8.916	14.956
2100.00	68.321	75.867	8.919	15.847
2200.00	68.674	76.282	8.921	16.739
2300.00	69.013	76.679	8.923	17.631
2400.00	69.341	77.059	8.924	18.524
2500.00	69.657	77.423	8.926	19.416
2600.00	69.962	77.773	8.927	20.309
2700.00	70.258	78.110	8.928	21.202
2800.00	70.544	78.435	8.929	22.095
2900.00	70.821	78.748	8.930	22.988
3000.00	71.091	79.051	8.931	23.881
3100.00	71.352	79.344	8.932	24.774
3200.00	71.606	79.627	8.932	25.667
3300.00	71.854	79.902	8.933	26.560
3400.00	72.094	80.169	8.933	27.453
3500.00	72.329	80.428	8.934	28.347
3600.00	72.557	80.680	8.934	29.240
3700.00	72.780	80.924	8.935	30.134
3800.00	72.998	81.163	8.935	31.027
3900.00	73.210	81.395	8.936	31.921
4000.00	73.417	81.621	8.936	32.814
4100.00	73.620	81.842	8.936	33.708
4200.00	73.818	82.057	8.936	34.602
4300.00	74.013	82.267	8.937	35.495
4400.00	74.202	82.473	8.937	36.389
4500.00	74.389	82.674	8.937	37.283
4600.00	74.571	82.870	8.937	38.176
4700.00	74.749	83.062	8.938	39.070
4800.00	74.925	83.250	8.938	39.964
4900.00	75.096	83.435	8.938	40.858
5000.00	75.265	83.615	8.938	41.751
5100.00	75.430	83.792	8.938	42.645
5200.00	75.593	83.966	8.939	43.539
5300.00	75.752	84.136	8.939	44.433
5400.00	75.909	84.303	8.939	45.327
5500.00	76.063	84.467	8.939	46.221
5600.00	76.215	84.628	8.939	47.115
5700.00	76.364	84.786	8.939	48.009
5800.00	76.510	84.942	8.939	48.902
5900.00	76.655	85.095	8.939	49.796
6000.00	76.797	85.245	8.939	50.690

THEMODYNAMIC FUNCTIONS OF FeO_2/C

$$\Delta H_{298}^\circ = -76.3 \text{ KCAL/MOLE}$$

T (°K)	$-(F-H_{298})/T$ (cal/mole °K)	S (cal/mole °K)	C_p (cal/mole °K)	H_{298}° (kcal/mole)
298.15	8.590	8.590	13.112	0
300.00	8.590	8.671	13.198	.024
400.00	9.153	12.953	16.294	1.520
500.00	10.303	16.768	17.810	3.233
600.00	11.664	20.101	18.704	5.062
700.00	13.083	23.032	19.306	6.964
800.00	14.493	25.640	19.750	8.916
900.00	15.864	27.947	20.104	10.911
1000.00	17.185	30.121	20.401	12.937
1100.00	18.451	32.078	20.662	14.990
1200.00	19.663	33.886	20.897	17.068
1300.00	20.822	35.567	21.114	19.169
1400.00	21.932	37.140	21.319	21.291
1500.00	22.996	38.617	21.514	23.432
1600.00	24.016	40.012	21.702	25.593
1700.00	24.996	41.333	21.885	27.773
1800.00	25.939	42.589	22.063	29.970
1900.00	26.847	43.787	22.237	32.185
2000.00	27.723	44.932	22.409	34.417
2100.00	28.569	46.029	22.578	36.667
2200.00	29.386	47.083	22.746	38.933
2300.00	30.178	48.098	22.912	41.216
2400.00	30.945	49.077	23.077	43.515
2500.00	31.690	50.022	23.240	45.831
2600.00	32.412	50.937	23.403	48.163
2700.00	33.115	51.823	23.565	50.512
2800.00	33.798	52.683	23.726	52.876
2900.00	34.464	53.518	23.887	55.257
3000.00	35.113	54.331	24.047	57.653
3100.00	35.746	55.122	24.206	60.066
3200.00	36.363	55.893	24.366	62.495
3300.00	36.966	56.645	24.525	64.939
3400.00	37.660	57.375	24.683	67.398
3500.00	38.344	58.083	24.840	69.871
3600.00	39.019	58.778	24.996	72.358
3700.00	39.670	59.462	25.150	74.858
3800.00	40.303	60.134	25.303	77.371
3900.00	40.920	60.795	25.455	79.896
4000.00	41.521	61.445	25.606	82.433
4100.00	42.107	62.084	25.756	84.981
4200.00	42.678	62.712	25.905	87.540
4300.00	43.236	63.330	26.053	90.109
4400.00	43.782	63.937	26.200	92.688
4500.00	44.314	64.534	26.346	95.277
4600.00	44.835	65.121	26.491	97.875
4700.00	45.345	65.698	26.635	100.482
4800.00	45.844	66.265	26.778	103.097
4900.00	46.332	66.822	26.920	105.720
5000.00	46.811	67.369	27.061	108.351
5100.00	47.280	67.906	27.201	110.989
5200.00	47.740	68.434	27.340	113.643
5300.00	48.191	68.952	27.478	116.303
5400.00	48.633	69.461	27.615	118.968
5500.00	49.068	69.961	27.751	121.638
5600.00	49.494	70.452	27.886	124.313
5700.00	49.913	70.934	28.020	126.993
5800.00	50.325	71.407	28.153	129.678
5900.00	50.729	71.872	28.285	132.367
6000.00	51.127	72.329	28.416	135.060

THERMODYNAMIC FUNCTIONS OF $ZrOCl(g)$

$$\Delta H_{f298}^{\circ} = -56.0 \text{ KCAL/MOLE}$$

T (°K)	$-(F-H_{298}/T)$ (cal/mol °K)	S (cal/mol °K)	C_p (cal/mol °K)	H_{298}° (kcal/mol)
298.15	66.906	66.906	12.738	0
300.00	66.906	66.985	12.755	.024
400.00	67.416	70.761	13.472	1.338
500.00	68.400	73.818	13.902	2.709
600.00	69.522	76.378	14.171	4.113
700.00	70.663	78.576	14.347	5.540
800.00	71.774	80.501	14.469	6.981
900.00	72.841	82.210	14.555	8.432
1000.00	73.856	83.747	14.618	9.891
1100.00	74.819	85.142	14.666	11.355
1200.00	75.734	86.420	14.702	12.824
1300.00	76.602	87.598	14.731	14.295
1400.00	77.427	88.691	14.755	15.770
1500.00	78.212	89.709	14.773	17.246
1600.00	78.960	90.663	14.789	18.724
1700.00	79.676	91.560	14.802	20.204
1800.00	80.360	92.407	14.813	21.685
1900.00	81.015	93.208	14.822	23.166
2000.00	81.644	93.968	14.830	24.649
2100.00	82.248	94.692	14.837	26.132
2200.00	82.829	95.382	14.843	27.616
2300.00	83.390	96.042	14.848	29.101
2400.00	83.930	96.674	14.852	30.586
2500.00	84.452	97.280	14.856	32.071
2600.00	84.957	97.863	14.860	33.557
2700.00	85.445	98.424	14.863	35.043
2800.00	85.918	98.965	14.866	36.530
2900.00	86.377	99.486	14.869	38.016
3000.00	86.823	99.991	14.871	39.503
3100.00	87.255	100.478	14.873	40.991
3200.00	87.676	100.950	14.875	42.478
3300.00	88.085	101.408	14.877	43.966
3400.00	88.484	101.852	14.878	45.453
3500.00	88.872	102.284	14.880	46.941
3600.00	89.250	102.703	14.881	48.429
3700.00	89.619	103.110	14.882	49.917
3800.00	89.980	103.507	14.883	51.406
3900.00	90.331	103.894	14.884	52.894
4000.00	90.675	104.271	14.885	54.383
4100.00	91.011	104.638	14.886	55.871
4200.00	91.340	104.997	14.887	57.360
4300.00	91.662	105.347	14.888	58.848
4400.00	91.977	105.690	14.889	60.337
4500.00	92.285	106.024	14.889	61.826
4600.00	92.587	106.352	14.890	63.315
4700.00	92.884	106.672	14.890	64.804
4800.00	93.174	106.985	14.891	66.293
4900.00	93.459	107.292	14.892	67.782
5000.00	93.739	107.593	14.892	69.272
5100.00	94.013	107.888	14.892	70.761
5200.00	94.283	108.177	14.893	72.250
5300.00	94.548	108.461	14.893	73.739
5400.00	94.808	108.739	14.894	75.229
5500.00	95.064	109.013	14.894	76.718
5600.00	95.315	109.281	14.894	78.208
5700.00	95.563	109.545	14.895	79.697
5800.00	95.806	109.804	14.895	81.186
5900.00	96.045	110.058	14.895	82.676
6000.00	96.281	110.309	14.896	84.166

THERMODYNAMIC FUNCTIONS OF $\text{ZrOCl}_2(\text{g})$

$$\Delta H^\circ_{f298} = -144.0 \text{ KCAL/MOLE}$$

T (°K)	$-(F-H_{298}/T)$ (cal/mol °K)	S (cal/mol °K)	C_p (cal/mol °K)	H_{298} (cal/mol)
298.15	76.175	76.175	16.808	0
300.00	76.175	76.279	16.835	.031
400.00	76.850	81.284	17.909	1.774
500.00	78.156	85.352	18.520	3.598
600.00	79.648	88.764	18.892	5.470
700.00	81.164	91.696	19.133	7.372
800.00	82.644	94.262	19.296	9.294
900.00	84.064	96.541	19.411	11.229
1000.00	85.416	98.591	19.495	13.175
1100.00	86.700	100.452	19.558	15.128
1200.00	87.918	102.156	19.607	17.086
1300.00	89.074	103.727	19.645	19.049
1400.00	90.174	105.184	19.676	21.015
1500.00	91.220	106.543	19.701	22.984
1600.00	92.219	107.815	19.721	24.955
1700.00	93.171	109.011	19.738	26.928
1800.00	94.083	110.140	19.752	28.903
1900.00	94.956	111.208	19.765	30.878
2000.00	95.794	112.222	19.775	32.855
2100.00	96.600	113.187	19.784	34.833
2200.00	97.375	114.107	19.792	36.812
2300.00	98.121	114.987	19.798	38.792
2400.00	98.842	115.830	19.804	40.772
2500.00	99.538	116.639	19.810	42.753
2600.00	100.210	117.416	19.814	44.734
2700.00	100.862	118.164	19.819	46.715
2800.00	101.492	118.884	19.822	48.697
2900.00	102.104	119.580	19.826	50.680
3000.00	102.698	120.252	19.829	52.663
3100.00	103.275	120.902	19.831	54.646
3200.00	103.836	121.532	19.834	56.629
3300.00	104.381	122.142	19.836	58.612
3400.00	104.912	122.735	19.838	60.596
3500.00	105.430	123.310	19.840	62.580
3600.00	105.934	123.869	19.842	64.564
3700.00	106.426	124.412	19.843	66.548
3800.00	106.907	124.941	19.845	68.533
3900.00	107.376	125.457	19.846	70.517
4000.00	107.834	125.959	19.848	72.502
4100.00	108.282	126.450	19.849	74.487
4200.00	108.720	126.928	19.850	76.472
4300.00	109.149	127.395	19.851	78.457
4400.00	109.569	127.851	19.852	80.442
4500.00	109.980	128.297	19.853	82.427
4600.00	110.383	128.734	19.854	84.412
4700.00	110.778	129.161	19.854	86.398
4800.00	111.166	129.579	19.855	88.383
4900.00	111.546	129.988	19.856	90.369
5000.00	111.918	130.389	19.856	92.354
5100.00	112.284	130.783	19.857	94.340
5200.00	112.644	131.168	19.858	96.326
5300.00	112.997	131.546	19.858	98.312
5400.00	113.344	131.918	19.859	100.297
5500.00	113.685	132.282	19.859	102.283
5600.00	114.020	132.640	19.860	104.269
5700.00	114.350	132.991	19.860	106.255
5800.00	114.674	133.337	19.860	108.241
5900.00	114.994	133.676	19.861	110.227
6000.00	115.308	134.010	19.861	112.213

THERMODYNAMIC FUNCTIONS OF ZrOF(g)

$$\Delta H_{f298}^{\circ} = -101.0 \text{ KCAL/MOLE}$$

T (°K)	-(F-H ₂₉₈ /T) (cal/mol °K)	S (cal/mol °K)	C _p (cal/mol °K)	H ₂₉₈ (kcal/mol)
298.15	65.273	65.273	12.346	0
300.00	65.273	65.749	12.365	.023
400.00	65.769	69.027	13.179	1.303
500.00	66.730	72.026	13.695	2.646
600.00	67.829	74.552	14.008	4.034
700.00	68.948	76.729	14.222	5.446
800.00	70.043	78.638	14.369	6.876
900.00	71.094	80.337	14.474	8.319
1000.00	72.096	81.866	14.552	9.770
1100.00	73.048	83.256	14.610	11.229
1200.00	73.952	84.529	14.656	12.692
1300.00	74.812	85.704	14.691	14.159
1400.00	75.629	86.793	14.720	15.630
1500.00	76.408	87.810	14.743	17.103
1600.00	77.150	88.762	14.762	18.578
1700.00	77.860	89.657	14.778	20.055
1800.00	78.539	90.502	14.791	21.534
1900.00	79.190	91.302	14.803	23.014
2000.00	79.815	92.062	14.813	24.494
2100.00	80.415	92.785	14.821	25.976
2200.00	80.993	93.475	14.828	27.459
2300.00	81.550	94.134	14.835	28.942
2400.00	82.088	94.765	14.840	30.425
2500.00	82.607	95.371	14.845	31.910
2600.00	83.109	95.954	14.850	33.394
2700.00	83.596	96.514	14.853	34.880
2800.00	84.067	97.054	14.857	36.365
2900.00	84.524	97.576	14.860	37.851
3000.00	84.967	98.080	14.863	39.337
3100.00	85.398	98.567	14.866	40.824
3200.00	85.817	99.039	14.868	42.310
3300.00	86.225	99.496	14.870	43.797
3400.00	86.621	99.940	14.872	45.284
3500.00	87.008	100.372	14.874	46.772
3600.00	87.385	100.791	14.876	48.259
3700.00	87.753	101.198	14.877	49.747
3800.00	88.112	101.595	14.878	51.235
3900.00	88.463	101.981	14.880	52.722
4000.00	88.806	102.358	14.881	54.210
4100.00	89.141	102.726	14.882	55.699
4200.00	89.468	103.084	14.883	57.187
4300.00	89.789	103.434	14.884	58.675
4400.00	90.103	103.777	14.885	60.164
4500.00	90.411	104.111	14.886	61.652
4600.00	90.712	104.438	14.887	63.141
4700.00	91.008	104.758	14.887	64.629
4800.00	91.297	105.072	14.888	66.118
4900.00	91.582	105.379	14.889	67.607
5000.00	91.860	105.680	14.889	69.096
5100.00	92.134	105.975	14.890	70.585
5200.00	92.403	106.264	14.890	72.074
5300.00	92.668	106.547	14.891	73.563
5400.00	92.927	106.826	14.891	75.052
5500.00	93.182	107.099	14.892	76.541
5600.00	93.433	107.367	14.892	78.030
5700.00	93.680	107.631	14.893	79.520
5800.00	93.923	107.890	14.893	81.009
5900.00	94.162	108.144	14.893	82.498
6000.00	94.397	108.395	14.894	83.988

THERMODYNAMIC FUNCTIONS OF $\text{ZrOF}_2(\text{g})$

$$\Delta H_{f298}^{\circ} = -234.0 \text{ KCAL/MOLE}$$

T	$-(F-H_{298}/T)$	S	C_p	H_{298}°
(°K)	(cal/mol °K)	(cal/mol °K)	(cal/mol °K)	(kcal/mol)
298.15	72.318	72.318	16.142	0
300.00	72.319	72.418	16.173	.030
400.00	72.970	77.263	17.450	1.717
500.00	74.239	81.244	18.195	3.502
600.00	75.694	84.605	18.653	5.346
700.00	77.179	87.504	18.951	7.228
800.00	78.632	90.048	19.153	9.133
900.00	80.028	92.313	19.297	11.056
1000.00	81.360	94.352	19.402	12.992
1100.00	82.627	96.205	19.480	14.936
1200.00	83.830	97.903	19.541	16.887
1300.00	84.974	99.469	19.589	18.844
1400.00	86.061	100.922	19.627	20.804
1500.00	87.098	102.277	19.658	22.769
1600.00	88.087	103.547	19.684	24.736
1700.00	89.031	104.740	19.705	26.705
1800.00	89.936	105.867	19.723	28.677
1900.00	90.803	106.934	19.738	30.650
2000.00	91.635	107.947	19.751	32.624
2100.00	92.435	108.911	19.762	34.600
2200.00	93.205	109.830	19.772	36.577
2300.00	93.947	110.709	19.790	38.554
2400.00	94.663	111.551	19.787	40.533
2500.00	95.355	112.359	19.794	42.512
2600.00	96.024	113.136	19.800	44.491
2700.00	96.671	113.883	19.805	46.472
2800.00	97.299	114.603	19.810	48.452
2900.00	97.908	115.299	19.814	50.434
3000.00	98.499	115.970	19.818	52.415
3100.00	99.073	116.620	19.821	54.397
3200.00	99.631	117.250	19.824	56.379
3300.00	100.174	117.860	19.827	58.362
3400.00	100.703	118.452	19.830	60.345
3500.00	101.218	119.026	19.832	62.328
3600.00	101.721	119.585	19.834	64.311
3700.00	102.211	120.129	19.836	66.295
3800.00	102.690	120.658	19.839	68.278
3900.00	103.157	121.173	19.840	70.262
4000.00	103.614	121.675	19.841	72.246
4100.00	104.060	122.165	19.843	74.231
4200.00	104.497	122.643	19.844	76.215
4300.00	104.924	123.110	19.846	78.199
4400.00	105.343	123.567	19.847	80.184
4500.00	105.753	124.013	19.849	82.169
4600.00	106.155	124.449	19.849	84.154
4700.00	106.548	124.876	19.850	86.139
4800.00	106.935	125.294	19.851	88.124
4900.00	107.313	125.703	19.852	90.109
5000.00	107.685	126.104	19.852	92.094
5100.00	108.050	126.497	19.853	94.079
5200.00	108.409	126.883	19.854	96.065
5300.00	108.761	127.261	19.855	98.050
5400.00	109.107	127.632	19.855	100.035
5500.00	109.447	127.996	19.856	102.021
5600.00	109.781	128.354	19.856	104.007
5700.00	110.110	128.706	19.857	105.992
5800.00	110.434	129.051	19.857	107.978
5900.00	110.752	129.390	19.858	109.964
6000.00	111.066	129.724	19.859	111.950

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APPENDIX B

ERRATA IN PREVIOUS REPORTS

A number of significant errors or omissions in presentation have been noted in the five quarterly reports issued under this contract. Corrections, including those previously given in the Fourth Quarterly Report, are as follows:

First Quarterly (15 September 1962)

p. 11 -- The species " $\text{TaCl}_5(\text{g})$ " has been omitted from the list on this page.

p. 16 -- N_x^c should be defined as moles of nozzle material as condensed phase per 100 grams of equilibrium mixture, including condensed phase.

p. 17 and Figures 1-8 -- the pressure used in these calculations was 1000 psia.

Second Quarterly (15 December 1962)

Volume I:

p. 22 -- The curve labelled " Al_2 " should be labelled " Al ", and the curve labelled " Al " should be labelled " Al_2O "; the unlabelled curve should be labelled " C_2 ".

p. 66 -- ΔH_{f298}^0 for $\text{WF}_5(\text{g})$ should be listed as -384 kcal/mole.

p. 82 -- The phrase at the top of the page should read "subtracting the amount not vaporized."

Volumes II and III:

In the detailed presentation of performance results, the values of "CF SEA LVL" and "CF VAC" for the throat condition (" EPSILON " = 1.000)

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are interchanged in every case on the "SHIFTING EXPANSION" summary sheet.
For example, the second table on page 43 of Volume II should read:

EPSILON - - - - -	CF SEA LVL	CF VAC
1.000	1.236	1.251
2.000	1.428	1.459
3.000	1.489	1.533
⋮	⋮	⋮

Third Quarterly (15 March, 1963)

p. 4 -- Brackets should surround the terms following T, as

$$[H_T - H_{298} - C_{p298} (T-298)]$$

p. 6 -- The symbol identification code should read

- o Southern Research
- Mezaki
- x K. K. Kelley

p. 33 -- The title for Figure 9 should have the words
"at 1000 psia" added.

p. 36 -- The title of the referenced publication should read
"Thermodynamic Properties of Inorganic Substances, V. High
Temperature Heat Contents of Fifteen Refractory Borides."

Fourth Quarterly (15 June 1963)

p. 3 -- The first sentence should include "HBO₂" in the list
of species, even though this system was not studied in detail.

p. 43 -- The final sentence on this page is incorrect, in that
the additivity rule does apply if "A_{xy}" is taken to be negative, rather
than arbitrarily zero. The correct value is:

$$A_{XY} = - \left(\frac{1}{K+1} \right) \frac{M_X}{M_{XY}}$$

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Fifth Quarterly (15 September 1963)

p. 5 -- The caption for the middle graph should read " BF_2 ".

p. 14 -- The final phrase on this page should read "the total pressure line and CO line are almost indistinguishable."

p. 19 -- The reference cited for contact angle measurements should be numbered "9".

Section 3, pp. 25 ff -- Some ambiguity is present in this section concerning the use of the terms "Denison model", "simplified Denison model", and "unmodified Denison model". As used in this section, "simplified Denison model" and "unmodified Denison model" are taken to be the same, that is, the special case of the Denison model derived in the Second Quarterly Report under this contract. (The original, more general model proposed by Denison is not limited to the assumption of equilibrium at the wall, and it does include allowances for blowing and for heat conduction into the wall.) The "modified Denison model" referred to by inference is one which was obtained by semi-empirical modification of the "simplified Denison model" to take into account blowing, heat loss, and non-unity Lewis numbers; this model has not been reported in detail.